Ab initio modeling of few-layer dilute magnetic semiconductors

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Abstract—We present a computational model to model the magnetic structure of two-dimensional (2D) dilute-magneticsemiconductors (DMS) both the monolayers and multilayers using first-principles density functional theory (DFT), as well as their magnetic phase transition as a function of temperature using Monte-Carlo simulations. Using our method, we model the magnetic structure of bulk, bilayer, and monolayer MoS_2 substitutionally doped with Fe atoms. We find that the out-of-plane interaction in bilayer MoS_2 is weakly ferromagnetic, whereas in bulk MoS_2 it is strongly anti-ferromagnetic. Finally, we show that the magnetic order is more robust in bilayer Fe-doped MoS_2 compared to the monolayer and results in a room-temperature FM at an atomic substitution of 14-16%.

I. INTRODUCTION

Recent discoveries of two-dimensional (2D) magnets CrI_3 [1] and $CrGeTe_3$ [2] have sparked great interest in their use in a plethora of applications ranging from spintronics [3], valleytronics [4], and advanced memories [5]. However, the low Curie temperature of experimentally discovered 2D magnets (45 K for CrI_3) impedes their use in any practical application. Thankfully, the possible span of 2D magnets is quite large [6].

One avenue of realizing 2D magnets is searching for 2D crystals that intrinsically have a magnetically ordered ground state [7–10]. Unfortunately, most of the experimentally discovered crystal 2D magnets either have a sub 100 K Curie temperature [1], [2], or their ground states are debatable, e.g., in monolayer VSe_2 some experimental reports claim it to have a ferromagnetic groundstate [11], whereas other works claim it to have a charge-density-wave groundstate [12], [13].

Another promising avenue of realizing 2D magnets is to magnetically dope conventional 2D materials [14–17]. Magnetically doped semiconducting 2D materials combine the properties of semiconductors and magnets and are called dilute-magnetic-semiconductors (DMS) [18], [19]. One of the advantages of DMS over intrinsically magnetic crystals is the ability to control their properties through external fields [20]. However, the design span of DMS is quite large, and experiments cannot be performed for all of them. Hence, theoretical guidance is desired.

In this work, we present a theoretical model of the magnetic order of 2D DMSs using ab initio density functional theory (DFT) calculations and Monte-Carlo (MC) simulations. We apply our method to monolayer and bilayer transition-metaldichalcogenides (TMDs): MoS_2 doped with Fe. We find that both monolayer and bilayer Fe-doped MoS_2 can result in a room temperature ferromagnet at a 14-16 % atomic substitution.

II. METHODOLOGY

A. Magnetic structure modelling



Fig. 1. The computational method for calculating the critical temperature of DMSs. Our model only takes the crystal structure as the input. We first model the magnetic structure using a Heisenberg Hamiltonian, whose parameters we obtain from the total energy DFT calculations. We then calculate the critical temperature using a Monte-Carlo (MC) algorithm.



Fig. 2. (a) Monolayer MoS_2 doped with three Fe atoms. (b) Bilayer MoS_2 doped with three Fe atoms. θ shows the azimuthal angle between the two Fe atoms in two layers of MoS_2 . We find the exchange interaction $J(r, \theta)$ between the dopant Fe atoms.

Figure 1 shows our computational model for modelling 2D DMSs which closely follows Refs. [21] and [17], to model the magnetic structure of doped DMS. Here, we use MoS_2 as an example to demonstrate the method, however, our method is general and can be applied on any 2D DMS.

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Fig. 3. (a) The J(r) of bilayer MoS₂ doped with Fe as a function of distance (r). (b) The J(r) of bulk MoS₂ doped with Fe as a function of distance (r). The dots show the possible position of Fe atoms within the cut-off circle.

First, we create a set of small supercells (*e.g.*, $4 \times 4 \times 1$ or $5 \times 5 \times 1$) of MoS₂ and substitutionally dope the supercells with two Fe atoms. We then perform total energy DFT calculations on these structures with various magnetic orientations. We fit a parameterized Heisenberg Hamiltonian to the DFT energies and obtain its parameters. The procedure is outlined next, which closely follows Ref. [17].

To model the exchange parameters of the Heisenberg Hamiltonian, we write the Heisenberg Hamiltonian as

$$H = -\sum_{i,j} \mathbf{S}_i J_{i,j} \mathbf{S}_j + D \sum_i (\hat{S}_i^z)^2.$$
(1)

Here, the first term is the exchange interaction term between the i^{th} and the j^{th} magnetic atom (dopant) with $\mathbf{S} = S_x \mathbf{x} + S_y \mathbf{y} + S_z \mathbf{z}$, as the magnetic moment vector. $J_{i,j}$ is the strength of the exchange interaction between the i^{th} and the j^{th} magnetic atoms and is a tensor as described in Ref. [21]. The second term is the onsite anisotropy term with onsite anisotropy strength D. Within our model, we assume $J_{i,j}$ tensor to be diagonal and rotationally invariant in-plane $J^{xx} = J^{yy} = J^{\parallel}$ and $J^{zz} = J^{\perp}$, with J^{\parallel} being the in-plane exchange interaction, and J^{\perp} being the out-of-plane exchange interaction.

We further model the $J_{i,j}$ as a function of distance J(r) using the functional form proposed in Ref. [17], and modify it to account for out-of-plane interactions using,

$$J(r) = J_{\rm in}(r)\cos^2(\theta) + J_{\rm out}(r)\sin^2(\theta).$$
⁽²⁾

Here, $J_{in}(r) = A^{\perp/\parallel} \sum_{i=0}^{3} c_i B_i(r) h(r_c - r) + c^{\perp/\parallel} \exp(-r/\lambda) h(r - r_c)$, h(r) is the Heaviside step function. r_c is the in-plane cut-off radius within which we approximate the J parameters using B-splines $B_i(r)$ [22] of order 3, and outside r_c we approximate them using an exponential decay $c^{\perp/\parallel} \exp(-r/\lambda)$. Because in the out-of-plane direction, the exchange intraction is through the Van-der-Waals gap, we assume an exponential decay: $J_{out}(r) = c_{out}^{\perp/\parallel} \exp(-r/\lambda_{out})$, with $c_{out}^{\perp/\parallel}$ and λ_{out} being the free parameters. θ is the azimuthal angle between dopants in

different layers [21] of a layered material (shown in Fig. 2 for bilayer MoS_2), for dopants in the same layer $\theta = 0$. For all materials in this work, we have considered the cut-off radius to be $r_c = 7$ Å.

Our method is computationally more efficient compared to the traditional $J_1 - J_2$ method [23] because going beyond the nearest-neighbor interaction in the $J_1 - J_2$ model increases the number of parameters as 2N, where N is the interaction range [23]. However, in our method, the number of free parameters remains fixed to eight even for interactions beyond fifth-nearest neighbors [17].

B. MC simulations

Using a Monte-Carlo (MC) algorithm [24], we study the phase change of the parameterized Heisenberg Hamiltonian for large (40 × 40) supercells doped with an atomic substitution of Fe atoms ranging from 6% to 18%. For each concentration, we average over 20 different dopant configurations (samples) to account for the configurational entropy. We start the MC simulation by assigning a starting magnetization ($M_{\rm sat} = \sqrt{S_x^2 + S_y^2 + S_z^2}$ with a random orientation [21]. From the MC simulation, we obtain the average magnetization ($M = 1/N_{\rm atom} \sum_{i=1}^{N_{\rm atom}} \sqrt{S_x^{i}^2 + S_y^i}^2 + S_z^{i}^2$) for $N_{\rm atom}$ numbers of dopants, and the susceptibility (χ). From the peak of the susceptibility for configurations with an average saturation magnetization: $\hat{M}[M/M_{\rm sat}] \ge 0.3$, we obtain the Curie temperature.

C. DFT calculations

All the ab-initio DFT calculations reported in this work were performed using the Vienna ab-initio simulation package (VASP) [25], [26]. For the ground state self-consistent field (SCF) calculations, we used a projector-augmented wave (PAW) potential [25] with a generalized-gradient approximation as proposed by Perdew-Burke-Ernzerhof (PBE) [27]. We have used a kinetic energy cut-off of 450 eV for our DFT calculations. The Brillouin zones were sampled using a Γ centred k-point mesh of size $[20/\alpha_1] \times [20/\alpha_2] \times [6/\alpha_3]$



Fig. 4. (a) Curie temperature of Fe-doped monolayer and bilayer MoS_2 as a function of doping concentration. The solid line shows the median, whereas the shaded region shows the 25th to 75th percentile variance in Curie temperature. The observed variation in Curie temperature is due to the configurational entropy. (b) Average magnetization per dopant atom of bulk, bilayer, and monolayer MoS_2 doped with Fe atoms, obtained from the MC simulation. The solid line shows the median, whereas the shaded region shows the 25th to 75th percentile variance in the average magnetization.

for $\alpha_1 \times \alpha_2 \times \alpha_3$ supercells. The TMD supercells doped with transition-metals were relaxed until the force on each of the ions was below $10 \text{ meV}/\text{\AA}$. The energy convergence criterion for the subsequent SCF calculations was set to 10^{-4} eV .

To take into account the strong electron correlations in the d orbitals of the dopant transition metals, we have used the DFT+U method [28]. We calculated the U for Fe atoms in MoS₂ using the linear-response method [29]. We found a U = 4 eV for the Fe atoms, which we have used in all subsequent DFT calculations.

III. RESULTS AND DISCUSSION

Figure 3 (a) shows $J(r, \theta)$ for Fe-doped bilayer MoS₂. The parameters for $J(r, \theta)$ are shown in Table I. We observe that the out-of-plane interaction is weaker than the in-plane interaction in Fe-doped bilayer MoS₂. Moreover, $J(r, \theta)$ is positive in both the in-plane and the out-of-plane direction, implying that the magnetic interaction is ferromagnetic (FM).

Figure 3 (b) shows $J(r, \theta)$ for Fe-doped bulk MoS₂. We observe that the out-of-plane interaction is weaker than the inplane interaction in Fe-doped bulk MoS₂. However, $J(r, \theta)$ is positive in the in-plane and negative in the out-of-plane direction, implying that the magnetic interaction is ferromagnetic (FM) in-plane and anti-ferromagnetic out-of-plane. Moreover, comparing bulk MoS₂ to the bilayer MoS₂, we find that the out-of-plane interaction is stronger in magnitude for the bulk compared to the bilayer MoS₂.

Figure 4 (a) shows the Curie temperature of bilayer and monolayer MoS_2 as a function of the fraction of atomic substitution of Fe atoms. We observe that for monolayer MoS_2 , the Curie temperature stays at 0 K for low atomic substitution (<13%), whereas, for bilayer MoS_2 , the Curie temperature shows a monotonic increase with increasing substitution. Moreover, we see that atomic substitution above 14% leads to room-temperature ferromagnetism for both the monolayer and the bilayer. Figure 4 (b) shows the saturation magnetization (M/M_{sat}) of the monolayer, bilayer, and bulk MoS₂ as a function of the fraction of atomic substitution of Fe atoms, obtained from the MC simulations. We observe that for bilayer MoS₂, the saturation magnetization is higher than monolayer and bulk MoS₂. For the bulk MoS₂, the saturation magnetization remains almost zero because bulk MoS₂ is an anti-ferromagnet in the out-of-plane direction. Therefore, the Fe dopants in different layers of bulk MoS₂ orient in the opposite direction, leading to an overall anti-ferromagnetic orientation with almost zero saturation magnetization.



Fig. 5. $J(r, \theta = 0)$ for bilayer and monolayer MoS₂ doped with Fe as a function of distance (r) between the in-plane dopants. The dots show the discrete J parameters calculated using the $J_1 - J_2$ model for the monolayer MoS₂. We see that the in-plane interaction at long-range is higher in bilayer compared to monolayer MoS₂, leading to a higher Curie temperature at lower fractions of atomic substitution.

Figure 5 shows the comparison of the in-plane exchange interaction $J(r, \theta = 0)$ between the Fe-doped bilayer and monolayer MoS₂. We see that the short-range interaction is stronger in the monolayer, whereas the long-range interaction is stronger in the bilayer. The strong long-range interaction in

 TABLE I

 Parameters of the Heisenberg Hamiltonian

Layer	$A_{\parallel} [{\rm eV}/\mu_{\rm B}^2]$	$A_{\perp} [{\rm eV}/\mu_{\rm B}^2]$	c_1	c_2	c_3	$D[{\rm eV}/\mu_{\rm B}^2]$	$c_{\rm out}^{\parallel} [{\rm eV}/\mu_{\rm B}^2]$	$c_{\rm out}^{\perp} [{\rm eV}/\mu_{\rm B}^2]$	$\lambda_{\rm out}[{\rm \AA}^{-1}]$
Monolayer	0.08	0.08	0.21	-0.09	-0.09	-1.6e-04	-	-	-
Bilayer	0.03	0.03	0.09	-0.17	-0.05	-1e-5	3e-10	6e-10	7.8e+03
Bulk	0.11	0.10	0.17	-0.13	-0.09	2.36e-4	-1.68e-03	-2.93e-03	5.17e+00

bilayer MoS_2 stabilizes the magnetic order at a lower atomic substitution leading to a non-zero Curie temperature in bilayer MoS_2 at a lower fraction of substitutions. However, the shortrange interaction becomes dominant at a higher fraction of substitution, which results in a comparable Curie temperature for both monolayer and bilayer MoS_2 . The weak long-range interaction in monolayer is compensated by stronger shortrange interaction at higher fractions of substitution.

IV. CONCLUSION

We have presented a model to calculate the magnetic phase transition of DMSs, both monolayer, and multilayer. Using the model, we have modeled the magnetic structure of Fedoped MoS_2 . We have calculated the atomic-substitutiondependent Curie temperature of the bulk, bilayer, and monolayer Fe-doped MoS_2 . We have shown that the out-of-plane interaction in bilayer MoS_2 is weakly ferromagnetic, whereas in bulk MoS_2 , the out-of-plane interaction is strongly antiferromagnetic. Finally, we have shown that the magnetic order is more robust in bilayer Fe-doped MoS_2 , compared to the monolayer, and results in a room-temperature FM at an atomic substitution of 14-16%.

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