Effects of dopant separation on electronic states and magnetism in monolayer MoS$_2$

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**A B S T R A C T**

The effects of vanadium (V) dopant on the electronic and magnetic properties of monolayer MoS$_2$ are investigated by first-principles calculation. The substitutionally doped V produces antiferromagnetic (AFM) or ferromagnetic (FM) states depending on the separation between V dopants. When the separation between V dopants is smaller than 6.38 Å and the maximum dopant concentration is 25%, the superexchange interaction between V atoms is stronger than the double exchange interaction between the localized V 3d orbitals and Mo 4d orbitals, resulting in the AFM state in monolayer MoS$_2$. However, the double exchange interaction between the V and Mo atoms becomes stronger than the superexchange interaction between V atoms if the separation between V dopants is larger than 9.57 Å when the maximum dopant concentration is 11.11%. Consequently, the FM state is observed from the monolayer MoS$_2$ and 100% spin polarization takes place if the separation between V atoms is further increased to 12.76 Å at a dopant concentration of 6.25%. The results suggest potential applications of monolayer MoS$_2$ as diluted magnetic semiconductors (DMS) in spintronics.

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1. Introduction

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have received much interest recently because of their extraordinary physical properties [1–5] spanning from semiconductors to superconductors and from non-magnetism to ferromagnetism, depending on the coordination environment and the number of d electrons in TM [6]. Among the different types of TMDs, monolayer MoS$_2$ has been extensively studied due to promising applications to field-effect transistors [7], lithium-ion batteries [8], photocatalysts, and so on [9]. Structurally, monolayer MoS$_2$ consists of a hexagonally arranged layer of Mo atoms sandwiched between two layers of S atoms in the D$_{3h}$ point group. Monolayer MoS$_2$ has been experimentally prepared by mechanical exfoliation and chemical vapor deposition (CVD) [10]. Although bulk MoS$_2$ has an indirect band-gap of 1.29 eV, the monolayer counterpart has a direct band gap of 1.81 eV due to the quantum confinement effect. The tunable band gap renders MoS$_2$ promising in nanoelectronic applications [11]. Recently, TMs and rare-earth doped MoS$_2$ have attracted much attention in the fields of 2D diluted magnetic semiconductors (DMS) and next-generation spintronic devices [12,13]. Based on annular dark-field scanning transmission electron microscopy (ADF-STEM) and electron energy loss spectroscopy (EELS), Robertson et al. [14] demonstrated substitution of Mo atoms in monolayer MoS$_2$ by Cr and V and the doped system exhibits magnetism. Ataca et al. [15] found that 3d transition metals adsorbed on 2D MoS$_2$ nanosheets could lead to local magnetic moments. Andriotis et al. [16] predicted that TM doping in 2D MoS$_2$ might result in ferromagnetic coupling. Mishra et al. [3] proved that the long-range ferromagnetism in Mn-doped system is mediated by an antiferromagnetic (AFM) exchange between the localized Mn d states and the delocalized p states of S, Se, and Te atoms. Zhang et al. [17] reported that Mn atoms could be incorporated into monolayer MoS$_2$ on graphene by in situ vapor phase deposition and the doped Mn alters the electronic states in monolayer MoS$_2$ substantially. Chen et al. [18]...
found that the magnetic anisotropy energy is sensitive to strain and MoS$_2$ underwent a spin reorientation from out-of-plane to in-plane magnetization at a critical strain of 3%. Ramasubramanian et al. [19] conducted first-principles calculation and Monte Carlo simulation to study the influence of the dopant concentration on the magnetic properties of Mn-doped monolayer MoS$_2$ and found that the Curie temperature might exceed the room temperature for dopant concentration between 10 and 15%, thereby demonstrating potential applications as atomically thin DMS. Cheng et al. [20] predicted that doping with Fe, Co, Zn, Cd, and Hg produces DMS properties in monolayer MoS$_2$, but V could not. However, Yun et al. [21] illustrated remarkable spin polarization in V-doped monolayer MoS$_2$. The discrepancy may be ascribed to the different interactions between dopants as well as between dopants and neighboring host atoms. Hence, TMs and rare-earth doping induced magnetism in monolayer TMDs is a complex process and not well understood.

Monolayer VS$_2$ itself actually exhibits a ferromagnetic behavior [22] and shares the same crystal structure as monolayer MoS$_2$ with a close lattice constant. Hence, substitutional V hardly affects the structural stability of monolayer MoS$_2$ [16,17]. In this work, the dopant concentration and dopant separation in V-doped monolayer MoS$_2$ are changed and first-principles calculation is performed to study the interactions between the dopants as well as between the dopants and neighboring host atoms. The influence on the electronic and magnetic states is evaluated. The results show that substitutional V can produce antiferromagnetic (AFM) or ferromagnetic (FM) states depending on the separation between V dopants. The transformation from FM to AFM states is discussed according to the exchange interaction.

2. Calculation details

First-principle calculation was carried out using MedeA-VASP [23–25] based on the plane-wave basis set by the projector-augmented wave (PAW) method [26,27]. The generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) scheme [24] was adopted for the exchange-correlation interactions. The valence-electron configurations of S, Mo, and V were $3s^23p^4, 4d^55s^1$, and $3d^34s^2$, respectively and the kinetic energy cutoff for plane-wave expansion was set to 480 eV. A vacuum layer 16 Å thick was added perpendicular to the monolayer MoS$_2$ to avoid the interaction between adjacent layers. The Brillouin-zone integration was sampled using a $7 \times 7 \times 1$ k-mesh according to the Monkhorst-Pack scheme [28] for structure relaxation and a $9 \times 9 \times 1$ k-mesh for single-point calculation. The structure was fully relaxed for an energy convergence of $1.0 \times 10^{-5}$ eV and force convergence of 0.01 eV/Å. Additionally, the DFT + U method with U in the range of 1–5 eV is adopted for comparison. The U parameters used in this work are referred to the values based on Refs. [3,16,29].

3. Results and discussion

3.1. Structural stability

Fig. 1a depicts the top and side views of the 1H-MoS$_2$ with one Mo atom substituted by V atom in each supercell and the $i \times j$ ($i=2,3,4,5; j=1,2,3$; $i \times j < 9$, $j$ is an integer) supercells are constructed to change the dopant concentration. The calculated lattice constant ($a_1 = a_2$) of monolayer MoS$_2$ is 3.17 Å, which is in good agreement with previous theoretical results [6,30,31]. Fig. 1b depicts the top view of the $5 \times 5$ supercell model with two substitutional V atoms. Five doping configurations are involved: (I) first-nearest neighboring, (II) second-nearest neighboring, (III) third-nearest neighboring, (IV) fourth-nearest neighboring, and (V) fifth-nearest neighboring. In order to estimate the structural stability of the V-doped MoS$_2$, the formation energies of V-doped MoS$_2$ are calculated as

$$E_f = E_{tot}(MoS_2+V) - E_{tot}(MoS_2) - E_V + E_{Mo},$$

in which $E_{tot}(MoS_2+V)$ is the total energy of the V-doped MoS$_2$, $E_{tot}(MoS_2)$ is the total energy of the pristine monolayer MoS$_2$, and $E_V$ and $E_{Mo}$ are the atomic energies in their stable bulks, respectively. The results are listed in Table 1. All the formation energies are positive and in the range between 2.03 and 2.10 eV indicative of endothermic reactions. These reactions are similar to the experiments described in Ref. [14].

Phonon dispersion is calculated to examine the dynamical stability of V-doped MoS$_2$. Fig. 2a presents the phonon dispersion curve of pristine monolayer MoS$_2$, in which three acoustical branches are separated by a gap from six optical branches. No imaginary frequency is available on all the nine branches in the whole Brillouin zone (BZ), demonstrating that monolayer MoS$_2$ is dynamically stable. Fig. 2b presents the phonon dispersion curve of the $Mo_9V_1S_{18}$ system with a dopant concentration of 6.25%, and there is also no imaginary frequency in the BZ. The width of the acoustical branches and highest frequency of the optical modes are unchanged, whereas the gap between the acoustical and optical branches decreases from 47 cm$^{-1}$ to 39 cm$^{-1}$ because of the mid-gap frequency. Fig. 2c shows the phonon dispersion curve of the $Mo_9V_1S_{18}$ system with a dopant concentration of 11.11% and...
Table 1
Separation (d) between V atoms according to the periodic boundary conditions when one Mo atom has been substituted by V atom for a dopant concentration x (%), supercell (i × j) fixed in the axis direction b, and formation energy (E_t (eV)).

<table>
<thead>
<tr>
<th>d_{d,v}</th>
<th>x</th>
<th>SuperCell</th>
<th>E_t</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.38 Å</td>
<td>8 × 2</td>
<td>2.099</td>
<td>4.17</td>
</tr>
<tr>
<td>9.57 Å</td>
<td>8 × 3</td>
<td>2.099</td>
<td>5.35</td>
</tr>
<tr>
<td>12.76 Å</td>
<td>5 × 4</td>
<td>2.099</td>
<td>6.25</td>
</tr>
<tr>
<td>15.95 Å</td>
<td>4 × 5</td>
<td>2.099</td>
<td>7.12</td>
</tr>
</tbody>
</table>

Fig. 2. Phonon dispersion of (a) Pristine monolayer MoS₂, (b) Mo_{15}V₁S_{32} system with a dopant concentration of 62.5%, (c) Mo_{8}V₁S_{18} system with a dopant concentration of 11.1%, (d) Mo₈V₁S₅ with a dopant concentration of 25%. The inset pictures are the corresponding structures used in the calculation.

there is still no imaginary frequency in the BZ. The width of the acoustical branches increases from 229 cm⁻¹ to 237 cm⁻¹ and the highest frequency of the optical modes decreases from 458 cm⁻¹ to 443 cm⁻¹. This affects the stability of the doped monolayer MoS₂ slightly when the dopant concentration is less than 11.1%. However, as shown in Fig. 2d, one acoustic branch becomes negative between Γ and M when the dopant concentration is increased to 25%, suggesting that the doping configuration becomes unstable at large dopant concentrations.

3.2. Electronic states and magnetism

Firstly, the influences of U parameters in the DFT+U method on the corrections to d electrons are analyzed. Fig. 3a displays the energy difference (ΔE) between the spin-polarized and unpolarized states as well as the magnetic moment in Mo_{15}V₁S_{32} as a function of U. All the ΔE values are negative, but the absolute value of ΔE increases with U values, indicating that spin-polarized states is more stable, in particular, for the larger U values. The magnetic moment changes with U values little. Fig. 3b displays the total density of states (DOS) of Mo_{15}V₁S_{32} calculated by DFT and by DFT+U (U=2.5 eV) for comparison. It is found that the DOS is nearly independent on whether the U parameter is involved or not. No matter DFT or DFT+U is adopted, the system is in the FM state and there is 100% spin polarization in the V-doped monolayer MoS₂, and the spin-up channel displays an appreciable gap (1.52 eV) but the spin-down DOS is across the Fermi level. The spin-up and spin-down channels are no longer symmetrical. The corresponding partial DOS of V 3d orbitals, the nearest Mo 4d orbitals, and the nearest S 3p orbitals calculated by DFT/DFT+U (U=2.5 eV) are displayed in Fig. 3c and d, respectively. The double exchange interaction is caused by hybridization between the V 3d orbitals and its nearest neighboring Mo 4d orbitals [3,16], and the double exchange interaction predicted by using the DFT+U method is almost the same as that by using the DFT method. The weak p-d hybridization between V and S is also evidenced from the PDOS. The insets of
Fig. 3. (a) Energy difference ($\Delta E$) between the spin-polarized and unpolarized states as well as the magnetic moment for Mo$_3$V$_1$S$_8$ as a function of U, (b) DOS of Mo$_3$V$_1$S$_8$ calculated by DFT/DFT+U, (c) Partial DOS of Mo$_3$V$_1$S$_8$ calculated by DFT, (d) Partial DOS of Mo$_3$V$_1$S$_8$ calculated by DFT+U.

Fig. 3c and d show the isosurfaces of the spin density ($\rho^+ - \rho^-$) calculated by DFT/DFT+U, in which the magnetic moment is mainly located on V and adjacent Mo atoms. The U value affects the magnetic moment distribution and magnetic coupling in the V-doped system only a little. Accordingly, the DFT method is mainly adopted for the following calculations.

When the doping concentration is increased to 11.11%, the spin-up and spin-down channels are also asymmetrical and some states are across the Fermi level in the spin-down channel characteristic of magnetism as shown in the upper panel in Fig. 4a. The total magnetic moment in each supercell is also 1 $\mu_B$. In the lower panel in Fig. 4a, the mid-gap states of the spin-down channel are mainly from V 3d orbitals and adjacent Mo 4d orbitals owing to the double exchange interaction. Fig. 4b shows the electronic states of the Mo$_3$V$_1$S$_8$ for a dopant concentration of 25%. However, Mo$_3$V$_1$S$_8$ has no band gap characteristic of a metal. The spin-up and spin-down DOS are symmetrical, suggesting no magnetic moments in the Mo$_3$V$_1$S$_8$. Taking into account the valence electron configurations of Mo 4d$^5$5s$^1$ and V 3d$^3$4s$^2$, holes will be introduced in the V-doped monolayer MoS$_2$ resulting in p-type doping. In addition, because of the small supercell of the Mo$_3$V$_1$S$_8$ system, the doped V may interact with itself due to the periodic condition. As aforementioned, the electronic states and magnetism of the V-doped MoS$_2$ depend on the dopant concentration and interaction between V and Mo atoms. Especially, when the doping concentration is larger than 11.11%, a competition between the double exchange interaction and the superexchange interaction takes place.

To further analyze magnetism for different dopant concentrations, we calculate the energy difference ($\Delta E$) between spin-polarized and spin-unpolarized MoS$_2$ with substitutional V for different doping concentration and the results are shown in Fig. 5a. $\Delta E$ is negative at small dopant concentration (<1.11%), implying that the spin-polarized state is more stable and the system has magnetism. In general, the absolute value of $\Delta E$ decreases with increasing dopant concentrations in a multistep mode, and the separation (d) between V dopants in the monolayer MoS$_2$ with different concentrations are the same in each step, as shown in the insets in Fig. 5a. For instance, the systems with dopant concentrations of 2.50%, 2.86%, and 3.33% show a similar $\Delta E$ (~36.76 meV) and the same separation between adjacent V atoms ($d_1 = 15.95$ Å) in the first step. If the concentration is larger than 11.11%, $\Delta E$ becomes positive. That is, the spin-unpolarized state is more stable and the system becomes non-magnetic. Fig. 5b displays the energy difference ($\Delta E$) between the spin-polarized and unpolarized states as a function of the separation between V atoms. All the $\Delta E$ values are positive and increase with the separation gradually, indicating that the spin-unpolarized states become more and more stable. Fig. 5c shows the energy difference between the spin-polarized and spin-unpolarized MoS$_2$ for steps 1–3 of i × j supercells. For a given j, the absolute value of $\Delta E$ increases with the number i, but is almost unchanged if i is larger than 5. So the magnetic properties of the V-doped MoS$_2$ depend strongly on the separation between V atoms as well as on the interaction between them.

The separation between V atoms is changed to analyze the interaction between V atoms. Fig. 6 presents the results of the $6 \times 6$
Fig. 4. Total DOS and partial DOS for (a) Mo$_8$V$_1$S$_{18}$ with a dopant concentration of 11.11%, and (b) Mo$_3$V$_1$S$_8$ with a dopant concentration of 25%.

Fig. 5. (a) Energy difference ($\Delta E$) between the spin-polarized and unpolarized states: (a) for different dopant concentrations, (b) as a function of the separation between V atoms, and (c) for the supercells of different sizes.

Fig. 6. (a) Isosurfaces plot showing the spin density ($p^+ - p^-$) of the four V-doped monolayer MoS$_2$ being FM states and (b) Isosurfaces plot showing the spin density ($p^+ - p^-$) of four V-doped monolayer MoS$_2$ being AFM states. The isosurface value is 0.003 e/Å$^3$ and Fermi level is denoted by the vertical dashed line.
supercell with V atoms separated by 9.57 Å. Fig. 6a shows the iso-
surface plots of the spin density $\rho \uparrow - \rho \downarrow$ of the system in the FM
state and V atoms have the same spin direction with both neigh-
boring V and Mo atoms. Fig. 6b shows the isosurface plots of the spin
density $\rho \uparrow - \rho \downarrow$ of the system in the FM state, in which V atoms
have an opposite spin direction with neighboring V atoms but the same spin direction with the neighboring Mo
atoms. According to the calculated exchange energy $E_{ex}$ between
the AFM and FM states of the supercell, the AFM state is more stable
but the $E_{ex}$ is only 7.10 meV. It is consistent with the reported results
[32]. In fact, a separation of 9.57 Å is so large that the interaction
between V dopants is weak and the double exchange interaction
between V and neighboring Mo atoms becomes dominant [33].
Consequently, the system is in the AFM state.

By further reducing the separation between V dopants, the double-V doped monolayer MoS$_2$ of different configurations
[Fig. 1b] are calculated to study the V–V interaction and influence
on magnetic properties. As shown in Fig. 7a, the exchange energy
$E_{ex}$ between the AFM and FM states is negative, and the absolute
value increases with decreasing separation, indicating that the AFM
state becomes more stable at smaller separation between adjacent
V dopants. Fig. 7b shows the isosurface plot of the spin density
$\rho \uparrow - \rho \downarrow$ of the V-doped monolayer MoS$_2$ for the double-doping
configuration III. V has an opposite spin direction with adjacent V
and Mo atoms. Figs. 7c and d present the isosurface plots of the spin
density $\rho \uparrow - \rho \downarrow$ of the V-doped monolayer MoS$_2$ of the configu-
rations IV and V, respectively. The two V atoms have the opposite
spin directions, but V has the same spin direction with almost all
the neighboring Mo atoms. All in all, the superexchange interaction
between V dopants becomes stronger than the double exchange
interaction between V and adjacent Mo atoms when the separa-
tion between V atoms is smaller than 6.38 Å. These results show
that the magnetic properties of V-doped MoS$_2$ are very sensitive
in the interaction between V atoms and neighboring Mo atoms and
depends on the separation between V atoms.

4. Conclusion

The electronic states and magnetism of V-doped MoS$_2$ mono-
layer are investigated by first-principles method based on DFT.
The magnetism of the V-doped MoS$_2$ monolayer changes with
the separation between V atoms. The V doped MoS$_2$ monolayer
behaves like a diluted magnetic semiconductor if the separation
between V dopants is larger than 9.57 Å. 100% spin polarization
is obtained at a separation of 12.76 Å for a dopant concentration
of 6.25%. However, the system transforms from a diluted magnetic
semiconductor to nonmagnetic metal as the separation between V
dopants is reduced because of the stronger superexchange interac-
tion between V atoms.

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