Interlayer ferromagnetism and insulator-metal transition in element-doped CrI$_3$ thin films

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The exploration of magnetism in two-dimensional layered materials has attracted extensive research interest. For the monoclinic phase CrI$_3$ with interlayer antiferromagnetism, finding a static and robust way of realizing the intrinsic interlayer ferromagnetic coupling is desirable. In this Letter, we study the electronic structure and magnetic properties of the nonmagnetic element (e.g., O, S, Se, N, P, As and C) doped bi- and tri-layer CrI$_3$ systems via first-principles calculations. Our results demonstrate that O, P, S, As, and Se doped CrI$_3$ bilayer can realize interlayer ferromagnetism. Further analysis shows that the interlayer ferromagnetic coupling in the doped few-layer CrI$_3$ is closely related to the formation of localized spin-polarized state. This finding indicates that isolated interlayer ferromagnetism can be realized at high doping concentration (larger than 8.33%). When the doping concentration is less than 8.33%, but larger than 2.08%, an insulator-metal phase transition can occur since the localized spin-polarized states percolate to form contiguous grids in few-layer CrI$_3$.

Introduction—. Two-dimensional(2D) magnetic semiconductors have attracted extensive attention due to the enormous potential for novel magneto-optic[1,2], magnetoelectronic[3–14], and spintronic devices[15–17]. As a representative 2D layered material, CrI$_3$ possesses its own unique physical properties. The bulk CrI$_3$ has two different structures, i.e., high-temperature monoclinic phase and low-temperature rhombohedral phase. The bilayer CrI$_3$ with rhombohedral stacking exhibits interlayer ferromagnetic coupling, while that with monoclinic stacking exhibits interlayer antiferromagnetic coupling[18–24], and their phase transition temperature is 220 K[25]. Thus, the magnetic order of CrI$_3$ is susceptible to the variation of layer thickness and stacking order. Previous first-principles calculations have predicted that interlayer magnetic coupling can be effectively modulated by stacking order in bilayer[18–20]. Later experiments[22,23] approved that different stacking orders can affect the observed magnetic states of CrI$_3$ in both bulk and few-layer CrI$_3$ systems.

In van der Waals layered systems, the relatively weak interlayer coupling indicates that the interlayer magnetic order can be easily tuned via external means. Indeed, it was experimentally reported that monoclinic bilayer CrI$_3$ can be transformed from interlayer antiferromagnetic to ferromagnetic coupling by applying electric gating[26,29]. A possible physical mechanism describing this magnetic transition is the formation of magnetic polaron, which was theoretically confirmed[30]. Besides above external electric gating, a natural question arises: whether it is possible to find a static and robust way of realizing the intrinsic interlayer ferromagnetic coupling in few-layer CrI$_3$? In addition, for semiconductor materials, the carrier doping concentration may destroy the physical properties. Therefore, it is desirable to realize the interlayer ferromagnetically-coupled few-layer CrI$_3$ while maintaining its semiconducting characteristics without introducing additional carriers.

In this Letter, we perform a systematic study on the magnetic and electronic properties of nonmagnetic-element doped few-layer CrI$_3$ by using first-principles calculation methods. We first show that the interlayer ferromagnetic coupling can be established in bilayer CrI$_3$ doped with C, N, O, P, As, or Se. We then find that the interlayer ferromagnetic coupling is intimately related to the formation of magnetic polaron. Especially for the As-doped bi- or tri-layer CrI$_3$, it can achieve higher Curie temperature and does not introduce extra carriers in the presence of increasing doping concentration within certain scale, therefore maintaining the system’s semiconducting properties. In addition, an insulator-metal phase transition occurs with the help of percolated spin-polarized states at low doping concentration.

Calculation Methods—. Our first-principle calculations were performed by using the projected augmented-wave method[51] as implemented in the Vienna ab initio simulation package (VASP)[32,33]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type was used to treat the exchange-correlation interaction[34]. In our calculations, the lattice constant of the high-temperature phase of CrI$_3$ was chosen to be $a_0=6.92$ Å[19]. A vacuum buffer space of 15 Åwas used to prevent the coupling between adjacent slabs. The kinetic energy cutoff was set to be 340 eV. With fixed supercells, all structures were fully relaxed. The van der Waals (vdW) force was taken
first study the possibility of element doping in bilayer CrI₃ phase and the substitution sites are labeled as I₁ and I₂. Formation energies of (b) O, S, Se, N and (c) P, As or C element-doped bilayer CrI₃ as a function of the host element chemical potentials.

into account by employing the Grimme’s method (DFT-D2) [32]. The Brillouin-zone integration was carried out by using 5 × 5 × 1 Monkhorst-Pack grids. Unless mentioned otherwise, GGA+U [36, 37] method was used with the on-site repulsion parameter $U = 3.9$ eV and the exchange parameter $J = 1.1$ eV [19], where $U$ is for the more localized 3d orbitals of Cr atoms. The Curie temperature $T_C$ was estimated within the mean-field approximation by using $k_B T_C = 2/3 J x$ [38], where $k_B$ is the Boltzmann constant, $x$ is the dopant concentration, and $J$ is the exchange parameter obtained from the total energy difference between ferromagnetic and antiferromagnetic configurations.

Experimental Possibility of Element Doping—. We first study the possibility of element doping in bilayer CrI₃, i.e., substituting I by nonmagnetic dopants. Some typical candidates of nonmagnetic dopants including O, S, Se, N, P, As and C are considered. As displayed in Fig. 1(a), there are two types of I-doping sites labelled as I₁ (at the surface) and I₂ (inside the interlayer). The formation energy was obtained by using the expression $\Delta H_F = E_{tot}^D - E_{tot} - \Sigma n_i \mu_i$, where $E_{tot}^D$ is the total energy of the system including one nonmagnetic impurity, $E_{tot}$ is the total energy of the system, $\mu_i$ is the chemical potential for the species $i$ (host atoms or dopants), and $n_i$ is the corresponding number that was added/removed from the system.

As displayed in Fig. 1(b), for O, S, Se, N substitutions at two I sites in the same CrI₃ layer, the formation energy is within the range of $−0.4$ to $1.5$ eV. It indicates that the I₁ substitutional site is preferred due to smaller formation energy than that at I₂ substitution. For example, N substitution leads to smaller formation energy (about $−0.6$ to $0.2$ eV) than those from O (about $−0.2$ to $0.2$ eV), S (about $0.4$ to $0.9$ eV) and Se (about $1.1$ to $1.4$ eV) substitution in the whole range of the accessible host element chemical potentials. However, for P, As, and C substitutions [see Fig. 1(c)], they have larger formation energies than those with O, S, Se or N dopants. In addition, we find that the I₁ substitutional site is preferred by P and C, while I₂ substitutional site is preferred by As. The formation energy shows that all candidate elements (except As) are more stable at I₁ position. The formation energy of As substituted I₂ site is positive (about $2.3$ to $2.7$ eV). It is noteworthy that C-doped ZnO has been experimentally fabricated even the estimated formation energy is about 5.3 eV [12], which is much larger than all element-doped CrI₃. Therefore, it is reasonable to believe that O, S, Se, N, P and As doped CrI₃ bilayer could be experimentally fabricated.

Magnetic Properties—. We now move to investigate the interlayer magnetic coupling of the doped CrI₃. Figure 2(a) displays the energy difference $\Delta E = E_{FM} - E_{AFM}$ between interlayer ferromagnetic and antiferromagnetic states for different element-doped bilayer CrI₃. As reported, the pristine bilayer CrI₃ exhibits interlayer antiferromagnetic coupling [18, 20]. The introduction of dopants except C and N leads to $\Delta E < 0$, indicating the formation of interlayer ferromagnetism. For the O, P, S, As, and Se substitution at I₁(I₂) site [see Fig. 2(a)], $\Delta E$ are respectively $-7.7(-2.2)$, $-3.6(-6.3)$, $-6.7(-4.0)$, $-49.7(-113.9)$, and $-5.4(-12.3)$ meV, indicating the interlayer ferromagnetic coupling. As a contrast, it maintains the interlayer antiferromagnetism in C or N doped case. Hereinbelow, we choose the I₂-site As-doped bilayer CrI₃ as an example to analyze the origin of the interlayer ferromagnetism.

FIG. 1. (a) Side and top views of crystal structures of high-temperature monoclinic bilayer CrI₃ phase and the substitution sites are labeled as I₁ and I₂. Formation energies of (b) O, S, Se, N and (c) P, As or C element-doped bilayer CrI₃ as a function of the host element chemical potentials.

FIG. 2. (a) Energy difference between interlayer ferromagnetic (FM) and antiferromagnetic (AFM) states. (b) Difference of interlayer distance between doping configuration and pristine CrI₃. (c) Charge difference between Cr atoms near doping site in the doped and pristine bilayer CrI₃. (d) Schematic illustration of spin-polarized state-mediated interlayer ferromagnetic coupling in doped bilayer CrI₃.
FIG. 3. Differential charge density of (a) pristine and (b) As-doped bilayer CrI₃. Spin density of (c) pristine and (d) As-doped bilayer CrI₃. Local density of states of (e) pristine and (f) As-doped bilayer CrI₃. Yellow and blue isosurfaces respectively represent charge accumulation and reduction. Red and green isosurfaces represent respectively spin up and spin down. Cr-d, I-p and As-p orbitals in each layer of CrI₃ are displayed.

For vdW magnetic materials, many studies have shown that the interlayer distance plays a crucial role in determining the interlayer magnetic coupling [43–46]. Thus, we first investigate the relationship between the interlayer distance and the energy difference $\Delta E$. Figure 2(b) displays the difference of interlayer distances between doped and pristine CrI₃. One can find that the interlayer distances in nearly all doped systems [except P-doped configuration at I₁ substitution] decrease with respect to the pristine case. Particularly, the interlayer distances in C, N, and O doped systems at I₁-site substitution shrink respectively about 0.14, 0.17, and 0.18 Å, which are much larger than that in the As-doped system. These together show that there is no obvious correlation between the strength of ferromagnetic coupling and the interlayer distance.

Another striking transport phenomenon is the insulating nature after doping. It is known that doping or gating can result in the ferromagnetism of semiconductors, but may also break the semiconducting property due to the carrier injection. Surprisingly, for O, P, S, As, and Se doped bilayer CrI₃, our results show that they exhibit both ferromagnetic and insulating features. In association with the experimental finding that different gate doping levels do not lead to n- or p-type conduction of bilayer CrI₃ dominantly with affected magnetic properties [28], it is believed that only insulated interlayer ferromagnetism in few-layer CrI₃ can be observed due to the formation of spin-polarized bound state at certain doping concentrations.
FIG. 4. (a-c-e-g) Schematic plots of two spin-polarized states at different distances ($d_{P-P}$) in As-doped bilayer CrI$_3$. (b-d-f-h) The density of states of ferromagnetic state and the energy difference between interlayer ferromagnetic (FM) and antiferromagnetic (AFM) states at different $d_{P-P}$ in As-doped bilayer. The shadow part indicates the formation of spin-polarized state.

property of two-As-atom doped bilayer CrI$_3$ at different As-As distances (i.e., various doping concentrations). For the nearest As-As distance $d_{P-P}=6.92$ Å, in comparison with density of states of only one-As-atom doped bilayer CrI$_3$ (see Fig. 3(f)), the spin-polarized states in Fig. 4(b) is more delocalized and only one spin-polarized states is formed [A more larger spin-polarized states is schematically plotted in Fig. 4(a)]. At this configuration (the estimated doping concentration is about 8.33%), it is a ferromagnetic insulator and the interlayer ferromagnetic coupling ($\Delta E = -177.0$ meV) becomes stronger than that ($\Delta E = -113.9$ meV) with only one-As dopant. When the As doping concentration decreases, from Figs. 4(c) and 4(e), we find that two spin-polarized states can be formed and percolated. In such percolated systems, they are p-type semiconductor with interlayer ferromagnetism (see Figs. 4(d) and 4(f)), but the ferromagnetic coupling becomes weaker than that of the insulating case. For longer As-As distance, two independent spin-polarized states are formed and the interlayer magnetic coupling almost disappears. For example, when the As-As distance $d_{P-P}$ is 13.17 Å, one spin-polarized state is about 6.6 Å. If the doping concentration is further decreased to 2.08%, our results indicate that an insulated and ferromagnetic bilayer CrI$_3$ can be formed again due to the independent spin-polarized states, similar to that in Fig. 3(f).

So far, we have shown that element doping in bilayer CrI$_3$ can induce interlayer ferromagnetism. The trilayer CrI$_3$ has weak interlayer ferromagnetic coupling [1]. Whether the element doping can enhance the interlayer ferromagnetism? By taking As-doping as an example in Fig. S2(a), three I substituted sites including I1, I2, and I3 are selected. The interlayer magnetic couplings and their relative stabilities are respectively displayed in Fig. S2(b) and Table S1. One can see that the state with interlayer ferromagnetic coupling is more stable than the other three states with interlayer antiferromagnetic coupling, which agrees well with the experimental observation [1]. One can find that the total energy of As substitution at I3 site is the lowest, indicating the most stable structure. Therefore, we show that the strong interlayer ferromagnetic coupling can also be established in trilayer CrI$_3$ via As doping.

Conclusions—. In summary, we demonstrate that the interlayer ferromagnetic coupling can be realized in both bilayer and trilayer CrI$_3$ by doping nonmagnetic elements. Our finding provides a new evidence that the interlayer ferromagnetic coupling in CrI$_3$ thin films may be related to the formation of spin-polarized states, and also provides an alternative scheme for the realization of
CrI\textsubscript{3} based ferromagnetic insulator.

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[51] See Supplemental Material at [URL will be inserted by publisher] for the density of states of the C, N, O, P, S, and Se doped bilayer CrI$_3$, four magnetic states related interlayer magnetic coupling and their relative stability.