Noncollinearity-modulated electronic properties of the monolayer CrI$_3$

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Introducing noncollinear magnetization into a monolayer CrI$_3$ is proposed to be an effective approach to modulate the local electronic properties of the two-dimensional (2D) magnetic material. Using first-principles calculation, we illustrate that both the conduction and valence bands in the monolayer CrI$_3$ are lowered down by spin spiral states. The distinct electronic structure of the monolayer noncollinear CrI$_3$ can be applied in nanoscale functional devices. As a proof of concept, we show that a magnetic domain wall can form a one-dimensional conducting channel in the 2D semiconductor via proper gating. Other possible applications such as electron-hole separation and identical quantum dots are also discussed.

Introduction.—Two-dimensional (2D) materials, such as graphene [1], MoS$_2$ [2], etc., have attracted much attention in experimental and theoretical studies owing to their distinct electronic [3], magnetic [4] and optical properties [5] and the potential applications in designing nanoscale functional devices [6, 7]. The latter requires effective manipulation of the physical properties like the conductance, the band gap and the magnetic orientation. The recent discovery of 2D magnetic semiconductors [8, 9] offers new opportunities in controlling the electronic properties by the magnetization [10] and vice versa [11]. Topological spin waves in the 2D honeycomb lattice have been discovered using neutron scattering [12].

Following the intriguing idea of van der Waals heterostructures [13, 14], the present studies of 2D magnetic materials are mostly focused on the ferromagnetic and antiferromagnetic coupling between neighboring layers. For instance in four layers of CrI$_3$, Song et al. observed a tunneling magnetoresistance, which was as large as $10^{5}\%$ [15]. The ferromagnetic and antiferromagnetic coupling in bilayer CrI$_3$ can be artificially switched by a gate voltage [11] or electrostatic doping [16]. The van der Waals spin valve has been proposed [17] consisting of bilayer graphene between two 2D ferromagnetic layers, where the electronic properties of the bilayer graphene strongly depend on the magnetic order of the two ferromagnetic layers. However, the magnetic coupling between 2D layers is much weaker than the in-plane coupling. Therefore tuning the in-plane magnetic order is more effective to modulate the electronic structure [18, 19].

In this paper, we use CrI$_3$ as an example of 2D magnetic materials and demonstrate the noncollinear magnetic order in the monolayer CrI$_3$ results in a novel modulation of its electronic properties. The physical origin of such modulation is revealed by first-principles calculations. The charge redistribution in noncollinear CrI$_3$ results in a noticeable increase of the work function compared with the collinear case. Thus both the conduction and valence bands are lowered down in the area of a magnetic domain wall or a Skyrmion. This energy shift can be employed, under proper gating, to generate local conducting channels, which can even be moved by a magnetic field or spin waves. The noncollinearity-modulated electronic structure of the monolayer CrI$_3$ may also be applied in electron-hole separation and creation of the identical quantum dots.

A prototype proposal.—The atomic structure of the

![Diagram of atomic structure of CrI$_3$](image)

FIG. 1. (a) Side and (b) top views of the atomic structure of a monolayer CrI$_3$. The blue and green balls represent chromium and iodine atoms, respectively. The red arrow $a_1$ (a$_2$) denotes the in-plane translational vector along zigzag (armchair) direction. (c) Schematic illustration of a magnetic domain wall in a monolayer CrI$_3$ and its influence on the electronic structure. The left (red) and right (blue) magnetic domains have the upward and downward magnetization, respectively. At the domain wall (white region), the noncollinear magnetization lowers down both the conduction and valence bands resulting in potential wells along the domain wall.
monolayer CrI$_3$ is shown in Fig. 1, where chromium atoms form a 2D hexagonal lattice and iodine atoms are located at both sides of this 2D lattice. The monolayer CrI$_3$ has perpendicular magnetic anisotropy [20] so the magnetization has either the upward or the downward orientation out of the 2D plane, as schematically plotted in Fig. 1(c). A magnetic domain wall is located at the boundary of the two magnetic domains, where there is a continuous transition of the magnetization orientation. As we will demonstrate later, the noncollinear magnetization in the area of a domain wall lowers down both the conduction and valence bands. In addition, the band that traps electrons forms a one-dimensional conducting channel in the insulating 2D sheet. In addition, the potential well in the conduction band can be excited into the conduction band leaving a hole in the valence band. Due to the potential gradient, the electron and hole would move towards the opposite direction, as illustrated in the inset of Fig. 2(a). The period of the SS is then defined by $\lambda = 2\pi / |\nabla \theta|$ and its wave vector $q = 2\pi / \lambda = |\nabla \theta|$. The calculation is carried out using the projected augmented waves method implemented in the Vienna ab initio simulation package (VASP) [22, 23]. The general gradient approximation is employed with the Perdew-Burke-Ernzerhof (PBE) type exchange-correlation functional. We sample the 2D Brillouin zone (BZ) by $10 \times 10$ $k$ mesh for the hexagonal primitive cell of CrI$_3$, which has two Cr and six I atoms. For larger systems, we keep the same density of $k$ points unchanged in the reciprocal space. A 25-Å-thick vacuum perpendicular to the monolayer is used in the calculation to prevent the interaction between neighboring unit cells. Spin-orbit coupling (SOC) is included in all the calculations unless otherwise stated.

Figure 2(a) shows the calculated magnetic moment of every atom in CrI$_3$ with a SS along the armchair direction and $\lambda = 24.3$ Å, which are plotted as a function of the relative coordinate along the SS direction. Every Cr atom has a magnetic moment $3 \mu_B$ while the magnetic moments of I atoms are negligible. These values are the same as in the collinear case. The polar angle $\theta$ of every Cr atom in the SS exhibits a linear dependence on the position. Note that both the direction and magnitude of the local magnetic moment are fully relaxed in the calculation. The above result indicates that the SS state is energetically stable.

The energy difference between a SS state and the collinear magnetization is plotted in Fig. 2(b) as a function of the wave vector $q$. The calculated values can be well described by the exchange interaction of the nearest pairs of Cr atoms ($J_1$) and of the next nearest neighbors ($J_2$). Specifically, we can write the energy difference $\Delta E$ for zigzag and armchair SSs, respectively, as

$$\Delta E = \frac{J_1}{2} \left( \cos \frac{qa}{2} - 1 \right) + \frac{J_2}{2} \left[ \cos (qa) + 2 \cos \frac{qa}{2} - 2 \right],$$

and

$$\Delta E = \frac{J_1}{4} \left( \cos \frac{qa}{\sqrt{3}} + 2 \cos \frac{qa}{2\sqrt{3}} - 3 \right) + J_2 \left( \cos \frac{\sqrt{3}qa}{2} - 1 \right).$$

Here $a = 7.0$ Å is the lattice constant, which equals to the length of the vector $a_1$ in Fig. 1. By fitting the calculated values of both zigzag and armchair SSs, we obtain the unified exchange parameters $J_1 = -10.5 \pm 0.6$ meV and $J_2 = -3.8 \pm 0.2$ meV, as the blue and red solid
Electronic properties of noncollinear CrI₃.—To study the influence of noncollinear magnetization on the electronic structure, we calculate the density of states (DOS) of CrI₃ without and with a SS state, which are shown in Fig. 3(a) and (b), respectively. For collinear case, the band gap is 0.88 eV and the work function is approximately 5.35 eV. The latter is defined by the energy difference between the highest energy of occupied states and the vacuum energy; see the inset of Fig. 3(c). For the zigzag SS state with $q = 0.3 \text{ Å}^{-1}$, the band gap has a slight variation of less than 0.1 eV, but the work function has a noticeable increase of 0.2 eV. Therefore both the highest occupied state and the lowest unoccupied state are shifted towards lower energy by the noncollinear magnetization.

The calculated energies of the highest occupied state and the lowest unoccupied state are plotted in Fig. 3(c). The energy of the lowest unoccupied state is lowered from -4.48 eV for the collinear case down to around -4.64 eV for both armchair and zigzag SSs. Moreover, this energy shift does not sensitively depend on the wave vector $q$; the empty circles and squares in Fig. 3(c) are located in a very narrow energy range of [-4.59, -4.67] eV. Analogously, the calculated energies of the highest occupied state are independent of the type of SSs and of the wave vector $q$. Compared to the highest occupied state of collinear CrI₃ at -5.37 eV, this energy with SSs is shifted down to approximately -5.57 eV by the presence of the noncollinear magnetization. We have artificially turned off the spin-orbit interaction in the calculation and found that the above energy shift still exists. In particular, the electronic states on both sides of the band gap contains mostly the minority-spin states. Such unique properties leads to the discovered energy shift, which is noticeable but not destructive.

The shift of both the conduction and valence bands of CrI₃ towards the lower energy caused by the noncollinear magnetization is the key result of this work. Such an unexpected energy shift originates from the noncollinearity-induced electron density redistribution, which in turn results in the increase of the work function. In Fig. 4(a), we plot the electron density difference in a cross section between the collinear CrI₃ and a zigzag SS state. Positive (negative) value indicates a larger (smaller) electron density in noncollinear CrI₃ than that of the collinear magnetization. The charge redistribution takes place mainly in the vicinity of Cr atoms and electrons move away from the central Cr plane. Near I atoms, the charge redistribution is relatively weaker and electrons also moves away from the central plane of CrI₃. This trend can be seen clearly if we perform the in-plane integration of the electron density difference, as shown in Fig. 4(b). The electron density redistribution essentially increases the surface dipole [24] on both sides of CrI₃. Owing to this enhanced surface dipole, the work function of noncollinear CrI₃ is larger than that of the collinear case. This is the physical reason why both the valence and con-
dots can be artificially created in such a system. ered conduction bands. With electrons trapped in these periodic potential wells of electrons because of the low-

Therefore, magnetic Skyrmions could be created because of the broken inversion symmetry. These Skyrmions can be realized by appropriate gating. For example, various metallic substrates may give rise to different gating effect, which has been studied in graphene and MoS$_2$ on metallic substrates [25]. Alternatively, ionic gating can be applied and is expected to have prominent effect [26]. A monolayer CrI$_3$ on a substrate with strong SOC would induce the so-called Dzyaloshinskii-Moriya interaction [27, 28] because of the broken inversion symmetry. Therefore, magnetic Skyrmions could be created or form a periodic lattice [29]. These Skyrmions can be periodic potential wells of electrons because of the lowered conduction bands. With electrons trapped in these potential wells under proper gating, identical quantum dots [30] can be artificially created in such a system.

Conclusions.—Using first-principles calculation, we have demonstrated that the noncollinear magnetization in a monolayer of 2D ferromagnet CrI$_3$ lowers down both the conduction and valence bands and hence increases the work function of CrI$_3$. The noncollinearity-induced modulation results from the charge redistribution, which enhances the surface dipole moment of CrI$_3$. This effect suggests a new and efficient way of tuning the electronic structure of 2D ferromagnetic materials by introducing, e.g., a magnetic domain wall or a Skyrmion, and shall have potential application in designing nanoscale functional devices made of 2D materials.

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