Emergent magnetic states due to stacking and strain in the van der Waals magnetic trilayer CrI$_3$

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Recently, three different magnetic states were observed experimentally in trilayer CrI$_3$ under pressure, including ferromagnetic (FM-)$\uparrow\uparrow\uparrow$, FM-$\downarrow\uparrow\downarrow$ and FM-$\uparrow\uparrow\downarrow$. To reveal the nature of these observed magnetic states, we studied the magnetic properties of four possible stacking structures in trilayer CrI$_3$: I (rhombohedral), II (monoclinic), III (hexagonal) and IV (triclinic). We find that all four stacking structures possess the FM-$\uparrow\uparrow\uparrow$ ground state. After applying a few strains, the FM-$\downarrow\uparrow\downarrow$ becomes the ground state in II and III structures, and the FM-$\uparrow\uparrow\downarrow$ is preferred in IV structure, while the FM-$\uparrow\uparrow\uparrow$ persists in I structure. Our results unveil that the three magnetic states observed in trilayer CrI$_3$ may correspond to different stacking structures with small tensile strains, which can well interpret the experimentally obtained pressure dependent interlayer coupling and Curie temperature. Our present study paves a way to design the magnetic multilayers with required magnetic states by tuning stacking and strain.

I. INTRODUCTION

After the recent discovery of ferromagnetic order in atomically thin layer CrI$_3$ and Cr$_2$Ge$_2$Te$_6$, two-dimensional (2D) van der Waals (vdW) ferromagnetic semiconductors have attracted much attention due to their exotic properties and potential applications in spintronics[3-7]. According to Mermin-Wagner theorem [8], the large magnetic anisotropy is required to stabilize the long-range ferromagnetism in 2D materials [9-12].

The magnetism in 2D materials can be sensitively controlled by external perturbations, such as electric field [10, 13-15], strain [16, 17] and stacking [18]. The stacking engineering is very promising, because there are many possible compositions to construct heterostructures with different 2D materials to enhance the magnetic properties[19-22], and to produce novel physical phenomena, such as the quantum anomalous Hall effect [23, 24], and axion insulators [25].

The 2D CrI$_3$, as an Ising-type ferromagnets with the Curie temperature of 45K in monolayer, has become a highlighted research hotspot[26-38]. For a few layers of CrI$_3$, it can be used as a spin-filter tunnel barrier possessing a giant tunneling magnetoresistance [26-29], and the magnetic interactions between adjacent layers can be tuned by electric gating, electrostatic doping and pressure[39-43]. Most of the theoretical studies on few-layers CrI$_3$ focused on bilayer [30-32, 35], and they show that rhombohedral stacking favors ferromagnetic (FM) interlayer interaction, while monoclinic stacking is beneficial to antiferromagnetic (AFM) interlayer interaction, which is in good agreement with the experimental observations[33]. Bulk CrI$_3$ is reported to be a ferromagnetic semiconductor with a band gap of about 1.2 eV [44], which maintains the rhombohedral stacking sequence with R3 space group symmetry with the temperature lower than ~220 K, and transforms to the monoclinic stacking with C2/m space group at higher temperature [45].

Recently, researchers have turned their attention to trilayer CrI$_3$. In 2019, Peng et al observed the rhombohedral stacking order with FM interlayer interaction (FM-$\uparrow\uparrow\uparrow$) at 10K in non-encapsulated trilayer CrI$_3$ [34]. However, Xu et al reported that the pristine exfoliated trilayer CrI$_3$ favors AFM interlayer interaction with spin antiparallel arrangement of every two adjacent layers (labeled as $\downarrow\uparrow\downarrow$), and under pressures, three magnetic states, i.e., FM-$\uparrow\uparrow\uparrow$, FM-$\downarrow\uparrow\downarrow$, and FM-$\uparrow\uparrow\downarrow$, can be obtained in trilayer CrI$_3$ [43]. It becomes important to uncover the nature of different magnetic states in trilayer CrI$_3$ observed in recent experiments.

In this paper, we systematically investigate the magnetic properties of the trilayer CrI$_3$ with four different stacking structures, including I (rhombohedral), II (monoclinic), III (hexagonal) and IV (triclinic). Our results show that the magnetic states FM-$\uparrow\uparrow\uparrow$, FM-$\downarrow\uparrow\downarrow$, and FM-$\uparrow\uparrow\downarrow$ experimentally observed in trilayer CrI$_3$ may come from different stacking structures with small tensile strain in trilayer CrI$_3$. The correspondence between the stacking structure and interlayer magnetic coupling could provide us a basis to design spintronic devices with desirable magnetic properties by adjusting the stacking order and strains.

II. COMPUTATIONAL METHODS

In our calculations, the projector augmented wave (PAW) method [46] based on the density functional theory (DFT) as implemented in the Vienna ab initio simu-
III. RESULTS

A. Four stacking orders in trilayer CrI₃

The primitive cell of monolayer CrI₃ consists of two magnetic Cr atoms and six I atoms with each Cr atom surrounded by six I atoms forming a distorted octahedron. The basic vectors \( \mathbf{a} \) and \( \mathbf{b} \) are along the zigzag direction of the honeycomb lattice composed of Cr atoms and the y-axis corresponds to the armchair direction as shown in Fig. 1(a). Here, we consider four different stacking structures in trilayer CrI₃: I (rhombohedral), which is the low-temperature phase of bulk CrI₃ with the upper layer of two adjacent layers always translating \( \sqrt{3}/3\mathbf{a} \) in the armchair direction (y-axis) relative to the lower layer; II (monoclinic), the high-temperature phase of bulk CrI₃ with the upper layer of two adjacent layers always moving \( 1/3\mathbf{a} \) in the zigzag (\( \mathbf{a} \)) direction relative to the lower layer; III (hexagonal), which is the primitive cell of the bulk CrI₃ with \( P3_112 \) space group, where the middle and top layers move \( 1/3\mathbf{a} \) along the zigzag direction \( \mathbf{a} \) and \( \mathbf{b} \) directions relative to the lower layer, respectively; IV (triclinic), which is constructed with the middle and top layer moving \( 1/3\mathbf{a} \) and \( \sqrt{3}/3\mathbf{a} \) along the zigzag (\( \mathbf{a} \)) and armchair (y) directions relative to the lower layer, respectively, as shown in Figs. 1(a)-(d).

To study the possible stacking structures of trilayer CrI₃, the interlayer exchange couplings are essential, which should be included in the model. Because the interlayer Cr-Cr distances (\( d'_1 \), \( d'_2 \) and \( d''_1 \)) are comparable with the intralayer second and third neighboring Cr-Cr distances (\( d_2 \), \( d_3 \)), as noted in Table S3 in Supplemental Materials, it is necessary to consider the intralayer second and third nearest-neighbor exchange couplings (\( J_2 \) and \( J_3 \)). In order to explore the relation between magnetic states and stacking structures of trilayer CrI₃, for each stacking structure we have studied four magnetic states FM→↑↑↑, FM→↑↓↓, FM↓↓↓, and AFM in our calculations, where FM (AFM) and ↑↑↑ (↑↓↓, ↓↓↓) represent the intralayer and interlayer exchange couplings, respectively, as shown in Fig. 1(e). By comparing the total energies of different spin configurations for every stacking structure, FM→↑↑↑ state is found to be the magnetic ground state for the above four stacking structures, and the experimental and calculated structural parameters are listed in Table I. Among the four stacking structures, I (rhombohedral) stacking structure possesses the lowest energy, and we select its lattice constant 6.962 Å as the initial lattice constant to investigate the effect of in-plane strain.

For the mixture of rhombohedral and hexagonal stackings, it contains the relative movement between adjacent layers in both armchair and zigzag directions, which is identical to the IV (triclinic) stacking order. For the mixture of hexagonal and monoclinic stackings, it contains the relative movement between adjacent layers in the zigzag direction, leading to II (monoclinic) and III (hexagonal) stacking structures.

B. Magnetic ground state

For simplicity, we apply the in-plane biaxial strain to investigate the strain effect on magnetic properties in trilayer CrI₃ for four different stacking structures. The in-plane biaxial strain is defined as \( \varepsilon = (a - a_0)/a_0 \),

| CrI₃          | \( a \) (Å) | \( d_1 \) (Å) | \( d_2 \) (Å) |
|--------------|-------------|--------------|--------------|
| Bulk (Exp. in[45]) | rhombohedral | 6.867 | 6.602 | 6.602 |
| (DFT)        | monoclinic  | 6.866 | 6.623 | 6.623 |
| Trilayer I(rhombohedral) | 6.962 | 6.706 | 6.706 |
| II (monoclinic) | 6.957 | 6.762 | 6.762 |
| III (hexagonal) | 6.960 | 6.755 | 6.755 |
| IV (triclinic) | 6.960 | 6.681 | 6.720 |
FIG. 1. The top and side views of (a) rhombohedral, (b) monoclinic, (c) hexagonal and (d) triclinic stacking structures in trilayer CrI$_3$. The yellow, green, and purple balls are the bottom, middle, and top Cr layers, respectively. (e) Schematic plot of four different spin configurations. FM and AFM denote the ferromagnetic and antiferromagnetic intralayer exchange couplings, respectively, and ↑↑↑, ↑↑↓ and ↓↑↓ represent the three possible interlayer spin orientations.

where $a_0$ and $a$ are lattice parameters without and with strain, respectively. For the trilayer CrI$_3$ with I (rhombohedral) stacking structure, the interlayer distance ($d$) decreases from 7.05 to 6.38 Å with the in-plane biaxial strain changing from -10% to 10% as shown in Fig. S1. With the increase of tensile strain, the FM-↑↑↑ spin configuration is always the magnetic ground state, and the energy difference between other spin configurations and FM-↑↑↑ is increased, indicating a more stable FM-↑↑↑ magnetic state with the decrease of interlayer distance. While with the increase of compressive strain, a magnetic phase transition from FM-↑↑↑ to AFM will occur when the compressive strain is larger than 6%. The similar magnetic phase transition from intralayer FM to AFM with the increase of compressive strain also occurred in monolayer CrI$_3$ [51]. For trilayer CrI$_3$ with II (monoclinic) and III (hexagonal) stacking structures, a tiny tensile strain will cause a magnetic phase transition from FM-↑↑↑ to FM-↓↑↓, and the reduced interlayer distance can stabilize the FM-↓↑↓ state. The change of magnetic phases under compressive strain for II and III structures is similar to that for the I (rhombohedral) stacking structure. The above I, II, III stacking structures cannot lead to the FM-↑↑↓ magnetic phase, which was observed in the experiment. To understand the stacking structure of the magnetic state FM-↑↑↓, which involves the both ferromagnetic and antiferromagnetic interlayer couplings in trilayer CrI$_3$, we have considered the IV (triclinic) stacking structure, which combines the structures of I and II (or III). Therefore, three magnetic states FM-↑↑↑, FM-↓↑↓ and FM-↑↑↓ observed experimentally in the trilayer CrI$_3$ [43] are all obtained in our calculations.

To study the relative stability of four stacking structures, we calculate the total energy of four stacking orders under different strains as shown in Fig. 2 (e), and find that in the range of compressive strain -6% to tensile strain 10%, the energy of the I (rhombohedral) stacking structure is always the lowest, and II (monoclinic) and III (hexagonal) structures have almost the same energy and is the highest. The total energy of the IV (triclinic) stacking structure is between that of I (rhombohedral) and II (monoclinic) structures, and it is interesting to note that the IV structure can be regarded as the combination of structures I and II. As shown in Fig. 2 (f), the electronic band gap shows a strong dependence on the magnetic states in trilayer CrI$_3$. In the range of 0∼10% compressive strain, four stacking structures I to IV possess the same magnetic ground states, and their band gaps are basically the same, and they all undergo a transition from semiconductor to metal with compressive tensile about -10%. In the range of 0∼10% tensile strain, the band gaps for stacking structures I-IV become different, and at the same time their magnetic ground states become different.
FIG. 2. The relative total energy as a function of strain for (a) rhombohedral, (b) monoclinic, (c) hexagonal and (d) triclinic stacking structures in trilayer CrI₃. For every stacking order, four different spin configurations FM-↑↑↑, FM-↓↑↓, FM-↑↓↓, and AFM are considered. The energy difference is defined as $\Delta E = E - E_0$, where $E_0$ is the energy of FM-↑↑↑ state at corresponding strain. (e) The relative total energy of II, III and IV stacking structures. $\Delta E$ is defined as $\Delta E = E - E_I$, where $E_I$ is the energy of I stacking structure under different strains. (f) Strain-dependent band gaps for four stacking structures in trilayer CrI₃.

C. Theoretical model analysis

To better understand the relation between the magnetic states and the stacking structures in trilayer CrI₃, we consider a Hamiltonian including intralayer and interlayer interactions $H = H_{\text{intra}} + H_{\text{inter}}$. The intralayer term $H_{\text{intra}}$ is written as

$$H_{\text{intra}} = H_0 + H_{\text{MAE}},$$

where $H_0$ is the isotropic Heisenberg model with $J_1$, $J_2$ and $J_3$ the intralayer the first-, second-, and third-nearest-neighboring exchange interactions, respectively, and $H_{\text{MAE}}$ is the magnetic anisotropy including the Kitaev-like exchange anisotropy and the single-ion anisotropy [52, 53]. The calculation details are provided in Supplemental Materials. For the two adjacent layers sliding $\sqrt{3}/3a$ along the armchair direction, the interlayer interaction $H_{\text{inter}}$ could be written as

$$H_{\text{inter}} = -\sum_{\langle i,i' \rangle} J_1' S_i \cdot S_{i'} - \sum_{\langle\langle i,i' \rangle\rangle} J_2' S_i \cdot S_{i'},$$

where $J_1'$ and $J_2'$ are the interlayer first- and second-nearest-neighbor exchange interactions, respectively, and $i$ and $i'$ represent Cr atoms in the adjacent layers. While for the two adjacent layers sliding $1/3a$ along the zigzag direction, the interlayer interaction $H_{\text{inter}}$ is written as

$$H_{\text{inter}} = -\sum_{\langle i,i' \rangle} J_2'' S_i \cdot S_{i'},$$

where $J_1''$ represents the interlayer nearest exchange interactions. The exchange couplings existing in stacking structures I to IV are marked in Fig. 3. Because the interlayer exchange couplings are included in the model for the stacking structures of trilayer CrI₃, the intralayer second and third nearest-neighboring exchange couplings $J_2$ and $J_3$ are also included, as discussed in subsection III.A. The values of $J_1$, $J_2$, $J_3$, $J_1'$, $J_2'$ and $J_1''$ can be extracted from DFT results by calculating the energies of several different spin configurations as shown in Figs. S2-S4 in Supplemental Materials, and the results for stacking structures I to IV under different strains are listed in Table II. By Eqs. (1) - (3), positive (negative) exchange integrals indicate a FM (AFM) interaction. When the applied strain is between -6%~10%, the calculated intralayer exchange couplings $J_1$ and $J_2$ are all positive values, which are much larger than that of $J_3$ which is negligible small. Table II and Fig. 2 show that $J_1$ is weakened and becomes a negative value when the compressive strain is larger than 6%. The intralayer nearest-neighboring exchange coupling is determined by the competition between AFM direct exchange and FM superexchange [54–56]. Decreasing Cr-Cr intralayer distance, the AFM direct exchange can be enhanced, and will dominate the intralayer exchange interaction.

D. Comparison with the experiment

Three different magnetic phases FM-↑↑↑, FM-↓↑↓, FM-↑↓↓ have been experimentally observed in the trilayer CrI₃ under the application of pressure [43]. For the measured FM-↓↑↓ magnetic phase, which corresponds to II (monoclinic) and III (hexagonal) stacking structures with a tiny tensile strain based on our DFT results, the critical field $(B_C)$ polarizing the FM-↓↑↓ state to FM-↑↑↑ state under different pressure is reported in the experiment [43]. Here, we adopt $4J''|S|^2 \approx -g\mu_B S B_C$ to roughly estimate the strength of the interlayer exchange
TABLE II. The magnetic ground state, intralayer and interlayer exchange couplings (meV) and magnetic anisotropy energy (meV/Cr) under different strains for four stacking structures. $J_1$, $J_2$, $J_3$, $J'_1$, $J'_2$ and $J''_1$ are labeled in Fig. 3, and a positive value indicates ferromagnetic coupling, whereas a negative value indicates antiferromagnetic coupling. Positive value of $E_{\text{MAE}}$ indicates the out-of-plane magnetization, otherwise the in-plane magnetization. The four stacking structures and different spin configurations are shown in Fig. 1.

| Trilayer CrI$_3$ | Strain | Ground state | $J_1|S|^2$ | $J_2|S|^2$ | $J_3|S|^2$ | $J'_1|S|^2$ | $J'_2|S|^2$ | $J''_1|S|^2$ | $E_{\text{MAE}}$ |
|------------------|--------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| I (rhombohedral) | -6%    | FM↑↑↑        | 2.09      | 2.26      | -0.89     | -0.43     | 0.57      | /          | 1.22      |
|                  | 0%     | FM↑↑↑        | 9.14      | 1.51      | -0.19     | -0.57     | 0.67      | /          | 0.63      |
|                  | 6%     | FM↑↑↑        | 11.23     | 1.12      | -0.05     | -0.46     | 0.82      | /          | 0.62      |
| II (monoclinic)  | -6%    | FM↑↑↑        | 2.06      | 2.18      | -0.70     | /          | /          | 0.13      | 1.22      |
|                  | 0%     | FM↑↑↑        | 9.21      | 1.34      | 0.06      | /          | /          | 0.01      | 0.61      |
|                  | 6%     | FM↓↑↓        | 11.18     | 1.02      | 0.14      | /          | /          | -0.41     | 0.29      |
| III (hexagonal)  | -6%    | FM↑↑↑        | 2.05      | 2.19      | -0.70     | /          | /          | 0.14      | 1.25      |
|                  | 0%     | FM↑↑↑        | 9.20      | 1.35      | 0.07      | /          | /          | 0.02      | 0.66      |
|                  | 6%     | FM↓↑↓        | 11.18     | 1.02      | 0.13      | /          | /          | -0.38     | 0.46      |
| IV (triclinic)   | -6%    | FM↑↑↑        | 2.06      | 2.18      | -0.69     | -0.50     | 0.59      | 0.13      | 1.23      |
|                  | 0%     | FM↑↑↑        | 9.28      | 1.33      | 0.06      | -0.63     | 0.70      | 0.01      | 0.61      |
|                  | 6%     | FM↑↑↓        | 11.20     | 1.01      | 0.13      | -0.53     | 0.83      | -0.39     | 0.45      |

FIG. 3. Interlayer interactions in (a) I (rhombohedral) with the first ($J'_1$) and second ($J'_2$) nearest-neighboring exchange couplings labeled, (b) II (monoclinic) with the nearest-neighbor ($J''_1$) labeled, (c) III (hexagonal) with the nearest-neighbor ($J''_1$) labeled and (d) IV (triclinic) with $J_1$, $J_2$ and $J''_1$ co-existing, respectively. The intralayer interactions including first ($J_1$), second ($J_2$) and third ($J_3$) nearest-neighboring exchange couplings between two Cr atoms are marked in (a).
values of their MAE are different.

The Curie temperatures $T_C$ for II (monoclinic) and III (hexagonal) stacking structures in trilayer CrI$_3$ with FM-$\downarrow\uparrow\downarrow$ state are simulated by Monte Carlo (MC) simulation based on a Hamiltonian described in Eqs. (1) - (3). A 40×40×1 supercell of hexagonal lattice with periodic boundary conditions is adopted, and the MC steps for each temperature is $10^6$. $T_C$ as a function of applied strain is plotted in Fig. 4(d). According to our calculations, in both monolayer and trilayer CrI$_3$, the multiples of experimental $T_C$ and simulated $T_C$ are close to 0.58 (see Supplemental Materials). Thus, to avoid the problem of overestimating $T_C$ in theoretical studies and better compare with the experimental results, the $T_C$ value obtained from the MC simulation for trilayer CrI$_3$ in our calculations are all rescaled by a factor of 0.58 to reproduce the experimental result. It is noted that the rescaled $T_C$ increases with the increase of tensile strain for small strain, which is qualitatively consistent with the experimental observation of $T_C$ [43].

![FIG. 4. Strain dependent interlayer exchange coupling $J^0_1|S|^2$ for (a) monoclinic and (b) triclinic stacking orders. The navy blue points are simulated from the experimental results [43]. (c) Strain-dependent magnetic anisotropy energy (MAE) which is defined as $E_{m||z}-E_{m||x}$ for four different stacking structures in trilayer CrI$_3$. A positive value of MAE indicates the out-of-plane magnetization, otherwise the in-plane magnetization. (d) Strain-dependent Curie temperature ($T_C$) for II (monoclinic) and III (hexagonal) stacking structures in trilayer CrI$_3$ by Monte Carlo simulations, which has been rescaled by a factor of 0.58 to reproduce the experimental results. The navy blue points in (d) are the experimental $T_C$ in trilayer CrI$_3$ with different applied pressures [43].](#)

E. Effect of electronic correlation

For 3$d$ orbitals in transitions-metal compounds, the electronic correlation parameter $U$ is important, and the estimated value for Cr atom in CrI$_3$ via the linear response approach [57] is about 3.35 eV (see Supplemental Materials). Thus, $U = 3$ eV is adopted in our above DFT calculations. To verify the robustness of our DFT results, we have also studied the magnetic phases of the four stacking structures under different strains with $U = 4$ eV. It is shown that our conclusion does not change for $U = 3$ and 4 eV. As shown in Fig. S8 in Supplemental Materials, for all four stacking structures, by applying a small tensile strain, the FM-$\uparrow\uparrow\downarrow$ magnetic state remains for I (rhombohedral) stacking structure, while it changes to FM-$\downarrow\downarrow\uparrow$ for II (monoclinic) and III (hexagonal) stacking structures, and it transforms to FM-$\downarrow\uparrow\downarrow$ for IV (triclinic) stacking structure. So, our conclusions do not change for reasonable parameter range of $U = 3 \sim 4$ eV. In addition, for the DFT+$U$ scheme with $U$ ranging from 0 to 4 eV, the picture of S=3/2 with all spin up $t_{2g}$ orbitals occupied is reasonable (see Fig. S2 in Supplemental Materials). The crystal-field splitting between $t_{2g}$ and $e_g$ orbitals of the trilayer CrI$_3$ with I (rhombohedral) stacking order can be roughly estimated as 3.62 eV, which changes slightly with the strain (see Fig. S3 in Supplemental Materials).

VI. CONCLUSION

In summary, by using the first-principles calculations, we find that the magnetic states in trilayer CrI$_3$ strongly depend on the stacking structures and interlayer distance. All four different stacking structures, including I (rhombohedral), II (monoclinic), III (hexagonal) and IV (triclinic), the FM-$\uparrow\uparrow\downarrow$ is the magnetic ground state. Under a small tensile strain, FM-$\uparrow\uparrow\downarrow$ is maintained in I (rhombohedral), while it transforms to FM-$\downarrow\uparrow\uparrow$ for II (monoclinic) and III (hexagonal), and changes to FM-$\downarrow\uparrow\downarrow$ for IV (triclinic). The three obtained magnetic states are consistent with the observations in the recent experiment. The intralayer and interlayer exchange couplings are extracted based on a Heisenberg-type Hamiltonian, which can well interpret the change of magnetic behavior in trilayer CrI$_3$. Our results also show that the band gap and MAE of trilayer CrI$_3$ are strongly dependent on the magnetic phases. This study presents a reasonable explanation for the experimental observations for the trilayer CrI$_3$, and paves a way to design multilayer devices with desired properties, such as novel magnetic states, suitable band gaps, and so on.
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