Prospects and Opportunities of 2D van der Waals Magnetic Systems

Meng-Chien Wang,* Che-Chun Huang, Chi-Ho Cheung, Chih-Yu Chen, Seng Ghee Tan, Tsung-Wei Huang, Yue Zhao, Yanfeng Zhao, Gang Wu, Yuan-Ping Feng, Han-Chun Wu, and Ching-Ray Chang*

The existence of spontaneous magnetization in low dimensional magnetic systems has attracted intensive studies since the early 60s and research remains very active even now. Only recently, magnetic van der Waals (vdW) systems down to a few layers have been broadly discussed for their magnetic order ground states at finite temperature. The naturally inherited layered structure of the vdW magnetic systems possessing onsite magnetic anisotropy from band electrons can suppress the long-range fluctuations. This provides an excellent vehicle to study the transition of magnetism to 2D limits both theoretically and experimentally. Here the current status of 2D vdW magnetic system and its potential applications are briefly summarized and discussed.

1. Introduction

It has been a long history ever since the origins for 2D magnetic systems were studied, in particular the transition of magnetism from bulk to 2D. The early predictions of the Mermin–Wagner–Hohenberg (MWH) theorem\cite{1,2} stated that for a finite, short range interaction in 2D systems, fluctuations of any kind can easily destroy long-range magnetic order at any finite temperature. It was also well known that the onsite anisotropy for a 2D Ising model can open a gap in the spin-wave spectrum and suppresses long range fluctuations.\cite{3,4} In Section 2, we review from both analytic theory and ab initio calculations points of view, the fundamental origins of spontaneous magnetization within a vdW magnetic system. The theory of 2D magnetism enlightens the possible way to find the 2D magnetic system in real world. Recently, intensive studies suggested that a curved 2D system introduces effective magnetic field, which can possibly counterbalance fluctuations.\cite{5} Last, current results of magnetic space group and ab initio calculations of 2D vdW magnetic system are summarized in Section 2.

The experimental realization of 2D magnetic system did not become possible until the invention of molecular beam epitaxy (MBE) in the late 1960s (Figure 1). It was the first time physicists can study how the transition of bulk to low dimensionality and its associated physics takes place in magnetic materials. Indeed, ultrathin film magnetism has been an active area of research since then and much of research works focused on fundamental physics of low dimensional magnetism.\cite{6} In thin film structure, many finite size effects emerge because the symmetry of bulk crystal structure breaks at film surface.\cite{7} One example is the magnetic moment enhancement of Fe and Co thin film relative to its bulk form.\cite{8-13} This effect is also observed in Co, Fe, and Ni nanoparticles whose magnetic moment is measured with the Stern-Gerlach experiment.\cite{14} This is in agreement with theoretical results obtained by ab initio calculations.\cite{15-20} The enhancement of moment can be explained by Stoner model of itinerant magnetism.\cite{21} Close to the surface of a material, the electronic band structure is different than that in the bulk. Here, the 3d band of transition metal becomes narrower near the surface because atoms of surface have reduced coordination number. The narrow energy band favors the exchange splitting and magnetic moment.\cite{21} As a result, the magnetic moment per
atom near the surface is larger than its value at the bulk. 3d electrons near the surface are more localized on the atomic site so their magnetic moment can be considered “atom-like,” as evidenced by the measured value of magnetic moment of small clusters by Billas et al.[14] This enhancement of magnetic moment per atom is much significant in thin film than in bulk for its large surface ratio. Other surface effects do also come into play, e.g., the decrease of interatomic distance at surface[22,23] and the increase of small orbital angular momentum at surface.[19,24] but their contributions are usually smaller. Reduced coordination of surface spins can even cause disordered spin structure in nanoparticles, which have antiferromagnetic interactions.[22,25-28] Nonetheless, enhancement of surface moments alone cannot provide the spontaneous magnetization from the MWH point of view.

Even though spontaneous magnetization in magnetic ultrathin films was frequently reported,[6] the physical origins of 2D magnetic system remain elusive. The effects of inherited anisotropy from the substrate, and induced anisotropy due to local defects are not considered within the MWH model. Moreover, long-range dipolar interactions of magnetic moments have also been neglected by this simple theory. To investigate the magnetic properties of a 2D system, a question naturally arises: What is the critical thickness for an ultrathin film to be regarded as a true 2D system? Experimentally, whether a film is 2D system or not can be determined by measuring the critical exponent of the film magnetization.[6,29-31] However, the data analysis is quite complicated by high structural disorder and island structures formed.[32,33] In the real world, experimental situations are not consistent with the ideal assumptions required in the MWH theorem.

In 2004, Novoselov et al. showed us a true 2D material exists by isolating single layer graphene from graphite.[34] Since then the family of 2D materials has been growing and a large variety of physical phenomena has been explored. As recent examples, emerging layered 2D transition metal dichalcogenides (TMDs) were found to display many intriguing properties in electronics, photonics, optoelectronics,[35,37] as well as magnetism.[38-40] The thin film spintronics utilizing the tunneling magnetoresistance (TMR)[41] and giant magnetoresistance (GMR)[42] has achieved great success. Since the discovery of spin transfer torque (STT),[43-45] the current-driven magnetization switching has been a hot research topic. In view of these success, wondering what spintronics device we can make using atomically thin magnetic materials is a natural question to ask. Indeed, low power spintronic devices based on 2D materials are frequently discussed recently.[46,47] Therefore, understanding the 2D vdW magnetic system is critical for designing practical spin logic and memory devices.[48-51] The vdW materials have a naturally layered structure and a highly crystalline character. In contrast to ultrathin magnetic films, the 2D flakes of layered vdW materials couple weakly to substrate. In addition, the previously mentioned effect of reduced coordination in ultrathin film is not serious in vdW materials because their interlayer coupling is the weak vdW interaction. Therefore, vdW magnetic materials can be considered as tailored-made testbeds for studying the pure dimensional crossover of magnetism from 3D to 2D. What is even better is that few layer vdW materials are sensitive to external stimulus such as gate voltage, light illumination, molecule adsorption, and neighboring material.[52-56] They provide unprecedented controllability of magnetism and give us possibilities to make heterostructures and devices for spintronic applications. Even though a lot of 2D magnetic vdW systems were reported from ab initio calculations (see Tables 1 and 2), only a few experiments were reported recently. In Section 3, we summarize the current status of 2D vdW magnetic system from an experimental point of view. Finally, the outlook and prospects of 2D vdW magnetic systems are discussed.
2. Low Dimensional Theory for Magnetization

2.1. The Mermin-Wagner-Hohenberg Theorem

Dimensionality and symmetry always play important roles in physics. The existence of exact solution is closely related to the dimension and symmetry of theoretical models. The most famous example in condensed physics is the Ising model. The 1D solution was obtained by Ising in 1924\[4\] and 2D Ising model was solved by Onsager about 20 years later in 1944.\[58\] In 1966, conclusions were made of the behavior of spontaneous magnetization that in 1D and 2D, there will be no breaking of spontaneous symmetry at finite temperature in continuous systems with sufficiently short-range interactions. This statement was also known as the MWH theorem since then.\[1,2\]

Here we briefly demonstrate the proof of MWH theorem. Other relevant contents can be found in many literature, see for example, ref. [59]. Starting from a quantum Heisenberg model with an external magnetic field \( b \)

\[
H = - \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + b \sum_i S_i^z \mathbf{R}_i \tag{1}
\]

Here, we assume that the exchange integrals \( J_{ij} \) decrease sufficiently fast with increasing distance \( |\mathbf{R}_i - \mathbf{R}_j| \). This is one of the kernel assumptions in MWH theorem, i.e., the interaction is
In momentum space, we choose where \( A \) and \( C \) are operators and \( H \) is the model Hamiltonian. Meanwhile, the Bogoliubov inequality (BI) for operators,\(^{[60]}\) through extending the Cauchy-Schwarz inequality to finite temperature, is given by:

\[
\frac{1}{2T} \langle [A, A^+] \rangle \langle [\{C, H\}, C^+] \rangle \geq |\langle [C, A] \rangle|^2
\]

where \( A \) and \( C \) are operators and \( H \) is the model Hamiltonian. In momentum space, we choose \( A = S_{i+k}^+ \) and \( C = S_{-k}^+ \), where \( S^± = S^z \pm iS^x \). Then the individual terms of BI are

\[
\langle [C, A] \rangle = 2 \langle S^z \rangle (k) = 2 \sum_i e^{ik \cdot r_i} \langle S_i^z \rangle = \frac{2N}{\delta H_B} M(T, b)
\]

and

\[
\langle [A, A^+] \rangle = 2N \sum_k \sum_{l} e^{i(k-l) \cdot (r_i-r_j)} \langle S_i^+ S_j^+ S_i^- S_j^- \rangle
\]

\[
= 2N \sum_k \left( \langle S_i^+ \rangle^2 + \langle S_i^- \rangle^2 \right) \leq 2N S(S+1)
\]

and

\[
\langle [C, H], C^+ \rangle \leq 4bN \left| \langle S_i^z \rangle \right| + 4 \sum_{ij} J_{ji} \left( 1 - \cos k \cdot (r_i - r_j) \right)
\]

\[
\times \left| \langle \frac{1}{N} \sum_{ii} \left( R_i^z \right) \rangle \right| \leq 4bM(T, b) + 4Nk^2QS(S+1)
\]

where \( S \) is the total spin and \( Q = \frac{1}{N} \sum_{ij} |R_i - R_j|^2 J_{ij} \).

### Table 1. Monolayer ferromagnet predicted by first principle calculation.

| Material      | Method used to calculate magnetic properties | Estimated \( T_c [K] \) | Electrical properties | Refs. |
|---------------|--------------------------------------------|------------------------|----------------------|-------|
| CrGeS₃        | DFT-PBE                                    | 161 (MF)               | Semiconductor        | \[121\] |
| CrSnTe₅       | HSE06                                      | 170                    | Semiconductor        | \[122\] |
| CrPSe₅        | DFT-PBE                                    | –                      | Semiconductor        | \[123\] |
| K₂CuF₄        | DFT-LDA+U                                  | –                      | Semiconductor        | \[124\] |
| MnS₂(1T)      | DFT-PBE+U                                  | 225                    | Semiconductor        | \[125\] |
| VS₂(2H)       | DFT-PBE+U                                  | 292                    | Semiconductor        | \[125\] |
| VS₂Te(2H)     | DFT-PBE+U                                  | 472                    | Semiconductor        | \[125\] |
| VS₂Se(2H)     | DFT-PBE+U                                  | 553                    | Semiconductor        | \[125\] |
| CrTe₂(1T)     | DFT-PBE                                    | 219.1 (MF)             | Metal                | \[126\] |
| NiCl₂         | DFT-LDA                                    | 205 (D)                | Semiconductor        | \[91\] |
| NiBr₂         | DFT-LDA                                    | 173 (D)                | Semiconductor        | \[91\] |
| Ni₃           | DFT-LDA                                    | 178 (D)                | Semiconductor        | \[91\] |
| CoCl₂         | DFT-LDA                                    | 134 (D)                | Semiconductor        | \[91\] |
| CoBr₂         | DFT-LDA                                    | 24 (D)                 | Semiconductor        | \[91\] |
| Co₃           | DFT-PBE                                    | 41                     | Semiconductor        | \[91\] |
| Cr₃           | DFT-PBE                                    | 49                     | Semiconductor        | \[91\] |
| Cr₃Br         | DFT-PBE+SOC                                | 29.7 (MF)              | Metal                | \[128\] |
| Mn₃Br₂Te₄     | DFT-PBE+U+SOC                              | 73                     | Semiconductor        | \[129\] |
| CrOCl         | DFT-GGA+U                                  | 160                    | Semiconductor        | \[130\] |
| CrOBr         | DFT-GGA+U                                  | 129                    | Semiconductor        | \[130\] |
| CrSCI         | DFT-PBE+U                                  | 150                    | Semiconductor        | \[130\] |
| CrSBr         | DFT-PBE+U                                  | 160                    | Semiconductor        | \[130\] |
| CrSili         | DFT-PBE+U                                  | 170                    | Semiconductor        | \[130\] |
| VS₂Se(2H)     | DFT-PBE+U                                  | 346 (MF)               | Metal                | \[131\] |
| VS₂Te(1T)     | DFT-PBE+U                                  | 165                    | Metal                | \[132\] |
| VS₂Se(1T)     | DFT-PBE+U                                  | 310                    | Metal                | \[132\] |
| Cr₂Se(1T)     | DFT-PBE+U                                  | 215                    | Metal                | \[132\] |
| Cr₂Te(1T)     | DFT-PBE+U                                  | 250                    | Metal                | \[132\] |
| Mn₂Te(1T)     | DFT-PBE+U                                  | 190                    | Metal                | \[132\] |
| Mn₂Se(1T)     | DFT-PBE+U                                  | 85                     | Metal                | \[132\] |
| Mn₂Te(1T)     | DFT-PBE+U                                  | 115                    | Metal                | \[132\] |
| LaBr₂         | DFT-GGA                                   | 235                    | Semiconductor        | \[120\] |

**MF:** mean field approximation, \( k_B T_c = 2(E_{AFM} - E_{FM})/3 \). *‘Calculated using exact solution of Ising model. Others are estimated by Monte Carlo Simulation.**

### Table 2. Monolayer half metal predicted by first principle calculation.

| Material      | Method used to calculate magnetic properties | Estimated \( T_c [K] \) | Calculated half metallic gap [eV] | Refs. |
|---------------|--------------------------------------------|------------------------|----------------------------------|-------|
| FeCl₂         | DFT-LDA                                    | 160½                  | 3.4                              | \[93\] |
| FeBr₂         | DFT-LDA                                    | 89½                   | –                                | \[93\] |
| Fe₃           | DFT-LDA                                    | 47½                   | –                                | \[93\] |
| TiCl₂         | HSE06                                      | 390                   | 0.6                              | \[96\] |
| MnS₅Se        | DFT-PBE+U                                  | 183                   | 1.15                             | \[122\] |
| VCl₃          | DFT-PBE+U                                  | 80                    | > 2                              | \[94\] |
| V₃           | DFT-PBE+U                                  | 98                    | > 2                              | \[94\] |
| Mn₃F₅         | DFT-PBE+U and HSE06                        | 450                   | ≈4(PBE+U)                        | \[95\] |
| MnCl₃         | DFT-PBE+U and HSE06                        | –                     | ≈3.2(PBE+U)                      | \[95\] |
| MnBr₃         | DFT-PBE+U and HSE06                        | –                     | ≈3.2(PBE+U)                      | \[95\] |
| Mn₃I₃         | DFT-PBE+U and HSE06                        | 720                   | ≈2.8(PBE+U)                      | \[95\] |

(1) Dirac half metals are shown in red color. (2) Half metallic gap is defined as the energy required to flip a spin at the Fermi level, that is the energy between the conduction band minimum of insulating spin channel and Fermi level. *‘Calculated using exact solution of Ising model. Others are estimated by Monte Carlo Simulation.**
Substituting what we have found in Equation (3) and summing over all the wave vectors of the first Brillouin zone we obtain, in the thermodynamic limit

\[ S(S + 1) \geq \left( \frac{M}{N g_B \mu_B} \right)^2 \sum_k \frac{1}{|bM| + k^2 N Q S(S + 1)} \]  

(4)

Changing the summation of \( k \) into integration, which can be done exactly in one and two dimension, we have

\[ |M(T, b)| \leq C_1 \frac{b^{1/3}}{T^{2/3}} \quad (1D) \]  

(5)

and

\[ |M(T, b)| \leq C_2 \left[ T \ln \left( \frac{C_3 + |bM|}{|bM|} \right) \right]^{-1/2} \quad (2D) \]  

(6)

where \( C_i \) (\( i = 1, 2, 3 \)) are constants. From the previous expressions of (5) and (6), we conclude that at \( T \neq 0 \), there will be no spontaneous magnetization \( M_{sp} \) in one and two dimensions, i.e.

\[ M_{sp} = \lim_{b \to 0} M(b, T) = 0 \]  

(7)

2.2. Thermal Excitation and Spontaneous Symmetry Breaking

In magnetic systems, we define an ordering phase, as when spins are correlated over a large enough distance. The correlation of spins is responsible for magnetization \( m_z \). It is expected that a system in its ordered ground state will be excited by rising temperature. When the temperature is higher than some critical temperature \( T_C \), generally larger than the typical coupling energy scale \( J \) in the quantum Heisenberg model, spins will be uncorrelated at large distances. The disappearance of magnetization \( m_0 \) describes a phase transition from order to disorder. For low dimensional magnetic systems, spins are easily excited, thus it is hard to form an ordered phase. One should note that the MWH theorem is based on lattice structures in 1D and 2D and does not take account of the anisotropic effect. Lattice with on-site anisotropy may show preference for spin ordering. Strictly speaking, thin film physics is not exactly the same physics as that described by the MWH theorem (Figure 2) for systems with substrate-inherited anisotropy. Nevertheless, ever since the discovery of graphene, weak vDW coupled system does provide an excellent possibility for the hosting of magnetism in a truly 2D system.

In field theory, spontaneous symmetry breaking is an important idea and a general phenomenon as well. An analogous theorem in relativistic field theory is proven by Coleman. Subsequent works following Coleman’s can be found in ref. [62] and references there in. In many articles, Coleman’s proof of the absence of Goldstone boson in 1 + 1 dimension is mentioned as a parallel to the MWH theorem, lending credence to what is also known as the Mermin-Wagner-Coleman theorem. From the point of view of mathematics, there are some similarities between MWH and Coleman’s proof. They both show the absence of symmetry breaking. However, MWH and Coleman theory are fundamentally different from the physics point of view. Coleman’s theory is that of one spatial plus one time degree of freedom, this is what we mean by “truly 2D” in the field theory. MWH theorem considers a lattice system in which the atoms are in one or two dimension but the spins may have z component. The Goldstone boson asserted by Coleman is also irrelevant to temperature. In other words, it can be applied even at \( T = 0 \). However the physics of MWH theorem tells us temperature plays an important role in low dimensions.

There are some aspects of the MWH theorem that should be emphasized here. i) The proof is valid only for \( T > 0 \). ii) Via the factor \( \exp(-\vec{k} \cdot \vec{R}) \) the proof also forbids long-range order in antiferromagnets. iii) MWH theorem cannot make any predictions for \( d > 2 \), but Roepstorff strengthened the proof to find an upper bound for magnetization in \( d \geq 3 \).

2.3. Magnetism on 2D Curved System

An ideal flat 2D surface normally will not appear in the real world, while in the meantime a lot of curved thin films or wrinkled vDW layers have been made. Surface roughness can induce global anisotropy because of the symmetry breaking and a periodically oscillatory structure (Figure 3). The magnetic moments on curved surfaces defined by simple smooth functions \( f(x, y) \) can produce a magnetic anisotropy axis along any direction because
of the long range dipolar interaction. This global surface anisotropy arising from periodic topography can compensate the fluctuation of magnetizations. Confinement along the normal direction of a curved space usually changes the equation of motion of the particles, leads to the quantization of the electronic states, and may induce a curvature-controllable geometric potentials, which is related to mean curvature and Gaussian curvature. For magnetism, the vector order parameters depend on real space. Theoretically, it is intuitive that geometric will produce another effect for magnetization after transforming to the curvilinear coordinates. This kind of curvature induced geometric potential can possibly induce local anisotropy or local effective magnetic field on curved surfaces. Magnetism in curved geometries has been rather intensively discussed recently and curvature induced local anisotropy and effective magnetic field can then counterbalance fluctuations and sustain spontaneous magnetization. Therefore magnetism in 2D curved system can also arise from the curvature induced anisotropy.

2.4. Magnetic Layer Group and 2D Magnetic Materials

There are 1651 magnetic space groups (MSGs) and 528 magnetic layer groups (MLGs) (see Table in ref. [73]) relevant to 2D magnetic materials. Here MSG and MLG will be briefly discussed. MSG is larger than space group, the study of the MSG needs the understanding of both space group symmetry and time reversal symmetry (TRS). In a periodic crystal, Brillouin zone mapping to wavefunction is analogous to a manifold mapping to another manifold. Such a mapping can have topological classification, which can be different under different system symmetry. Therefore, for the past two decades, physicists have been passionate about searching for different topological invariant with different symmetry constrain.

MSGs and MLGs can be roughly divided into four types:

Type1: only unitary spatial symmetry is considered, \( M = G \), \( G \) is original space group.
Type2: (gray group): has both original space group symmetry and time reversal symmetry, \( M = G + GT \), \( T \) is TRS operator.
Type3: (black and white space group): First take a subgroup element (\( H \)) from an original space group (\( G \)), and then with the addition of \( G - H \) by multiplying with TRS operation. In other words, \( M = H + (G - H)T \), \( H \) is a subgroup of \( G \).
Type4: A certain \( G \) is multiplied by a pure translation operation (\( t \)) and multiplied by the TRS operation (\( T \)). Finally, the original space group is added to obtain the Type4 magnetic space group. \( M = G + TtG \), \( t \) is a pure translation operation.

The naming methods of MSG and of MLG are the same, details can be found in ref. [73].

2.5. Ab Initio Calculations for 2D Magnetic Systems

First-principle calculation is a powerful theoretical simulation method to calculate the ground state energy, electronic structure, as well as other physical properties of a material. With the help of MWH theorem discussed in the previous paragraphs, one can apply ab initio calculations to identify the potential new 2D magnetic materials. Since first-principle calculation does not have any adjusting parameters, it has been used to predict new 2D materials and study the physical phenomena of 2D materials. Here we review the first-principle studies of magnetic properties in 2D materials.

Although many methods have been suggested to induce magnetism in nonmagnetic materials (see induced magnetism in nonmagnetic 2D material section in this article), only a few are realized experimentally and whether the defect induced local magnetic moments give rise to long-range magnetic order is debatable. Recently discovered ferromagnetism in monolayer CrI\(_3\) bilayer CrGeTe\(_3\) and antiferromagnetism in monolayer FePS\(_3\) has triggered intense studies on finding magnetic 2D materials. Given many bulk vdW magnetic crystals we have known for a long time, a lot of first principle studies have been launched recently to find magnetism in the monolayer counterpart of these bulk materials or any similar structures.

The standard procedure of first principle studies starts with obtaining the optimized crystal structure of the monolayer materials. The dynamical stability and thermal stability of these
Monolayers are usually examined by calculating phonon dispersion and performing molecular dynamics simulation, respectively. The exfoliation energy from their bulk counterpart is often calculated, since the weak exfoliation energy and the robust structure stability are closely related to the practicality of experimental realization of predicted 2D magnets. To study the magnetism, several types of magnetic ordering are considered, along with the nonmagnetic one (non-spin-polarized calculation). After self-consistent calculation, the phase with the lowest energy is the ground state. As previously mentioned, long-range magnetic order in two dimensions can be stabilized by uniaxial magnetic anisotropy. Therefore, calculating magnetic anisotropy energy (MAE) is crucial for justifying the prediction of monolayer magnet. The MAE is obtained by calculating the energy difference between phases in which initial spins are placed along orthogonal directions. It should be emphasized that including spin–orbit coupling (SOC) is necessary for calculating the MAE for 3d transition metal compounds since the orbital moment of 3d electron is almost completely quenched. The magnetic exchange constants are estimated by fitting the energy of adopted magnetic configurations to classical Heisenberg model

\[
H = -J_1 \sum_{i,j \in \text{NN}} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{i,j \in \text{2ndNN}} \mathbf{S}_i \cdot \mathbf{S}_j - J_3 \sum_{i,j \in \text{3rdNN}} \mathbf{S}_i \cdot \mathbf{S}_j
\]

NN: nearest neighbor

After obtaining exchange constants, Curie temperature is usually estimated by Monte Carlo simulation. We mainly focus on the magnetic properties of these predicted monolayer magnets.

Transition metal (TM) halides are one big class of the theoretical predicted monolayer ferromagnets. In TM halides, the nearest neighbor exchange interaction is determined by the competition of direct exchange interaction with superexchange interaction mediated by halogen anions. The strength and sign of these interactions strongly depends on the orbital occupation, namely electronic configuration of the TM atoms. Monolayer TM dihalides is composed of a triangular net of TM atoms (Figure 4a) in edge sharing octahedral structure, the corresponding ligand field created by halogen atoms splits 3d orbitals of TM into well-known eg (d\(_{x^2-y^2}\), d\(_{z^2}\)) and t\(_{2g}\) (d\(_{xy}\), d\(_{xz}\), d\(_{yz}\)) orbitals. The eg orbitals directly point toward the halogen atoms thus have higher energy than the t\(_{2g}\) orbitals. The low-lying t\(_{2g}\) orbitals of neighboring TM atoms have significant overlaps since they point between halogen atoms, resulting in strong AFM direct exchange. Botana and Norman systematically studied the magnetic properties of monolayer TM dihalides MX\(_2\) (M=V, Mn, Fe, Co, Ni; X=Cl, Br, I). The calculated ground state of monolayer VX\(_2\) and MnX\(_2\) is antiferromagnetic. Kulish et al. also found antiferromagnetic ground state for monolayer 1T CrX\(_2\). These results are in accordance with the strong t\(_{2g}\)–t\(_{2g}\) direct exchange. The stripe magnetic order is adopted for calculating the energy of AFM state in these studies. However, it should be noted that the actual magnetic pattern for these single layer materials may be more complicated, as AFM exchange interaction in triangle lattice usually leads to frustration effect. As an example, bulk VCl\(_2\) has a noncollinear 120° in layer order. Botana et al. predicted that CoCl\(_2\), CoBr\(_2\), FeX\(_2\), and NiX\(_2\) are monolayer ferromagnets. This can be understood in terms of the competition between the t\(_{2g}\)–t\(_{2g}\) direct exchange and eg–eg superexchange. According to the Goodenough–Kanamori rules for superexchange interaction, the eg–eg superexchange is ferromagnetic when the cation–anion–cation angle is 90 and this interaction increases with decreasing unpaired electrons in t\(_{2g}\) orbitals. By contrast, the t\(_{2g}\)–t\(_{2g}\) direct exchange decreases when the number of unpaired electrons in t\(_{2g}\) goes down, resulting in the dominance of superexchange interaction in late transition metal halides and ferromagnetic ground state for CoCl\(_2\), CoBr\(_2\), FeX\(_2\), and NiX\(_2\). Furthermore, the MAE calculated show that all monolayer MX\(_2\) has out of plane anisotropy, which meets the requirement for 2D magnetism.

Possible realization of half metallicity in 2D is very exciting because 2D half metals can be used as a spin filter in nanospintronic...
The electronic structure of FeX shows half metallic character with GGA (generalized gradient approximation), with a large gap in majority spin channel and metallic nature in minority spin channel. Moreover, the half metallicity in FeX is preserved when intra-atomic Coulomb repulsion U is included in the calculation, which is significant since U is widely used to correctly take into account strong electron-electron correlation of 3d electrons in TM.\cite{101,104} However, when SOC and U are simultaneously included, a gap opens up in the minority spin channel of FeCl\textsubscript{2} when U exceeds 3 eV. The opening of the gap can be explained by the occurrence of Jahn-Teller distortion\cite{91,105} in FeX\textsubscript{2}. Compression of FeX\textsubscript{2} octahedra along the c axis of FeX\textsubscript{2} takes place because the distortion lowers the energy of Fe\textsuperscript{2+} which has a triply degenerate ground state (d\textsuperscript{4}).\cite{105} The distortion splits t\textsubscript{2g} orbitals into low lying doubly degenerate e\textsubscript{g}* and high lying a\textsubscript{1g}, where e\textsubscript{g}* has the form\cite{90}

\[
e_{\text{g}*} = \pm \frac{1}{\sqrt{3}} \left( |xy| + e^{\pm \frac{\pi}{2}} |xz| + e^{\pm \frac{\pi}{2}} |yz| \right)
\]

The expectation value of c-axis angular momentum for the e\textsubscript{g}* orbitals is \pm 1. Therefore, degeneracy of e\textsubscript{g}* is broken upon the inclusion of SOC. Since the splitting increases with U, a gap opens up when U becomes larger. This picture is further supported by the electronic structure of CoCl\textsubscript{2} which already has a half metallic nature. In A-type antiferromagnet whose spin lies in plane.\cite{100,106} The uniaxial anisotropy again ensures the stabilization of inplane magnetic order down to monolayer. Ferromagnetism is found to be maintained in experimentally exfoliated few layer CrBr\textsubscript{2}.\cite{109} Note that although monolayer CrF\textsubscript{3} is found to be dynamically and thermally stable by first-principle calculation, bulk CrF\textsubscript{3} does not have vdW-type layered structure.

Dirac half metallicity, with a gap in one spin channel and a Dirac cone in the other spin channel, was first proposed by Ishizuka and Motome using Kondo lattice model.\cite{110} Monolayer TM trihalides are possible candidates for exhibiting Dirac half metallicity because of their graphene-like honeycomb lattice. Sun and Kioussis\cite{95} predicted that monolayer MnX\textsubscript{3} (X=F, Cl, Br, I) are Dirac half metal. The Fermi velocity of MnX\textsubscript{3} is about 10\textsuperscript{6} m s\textsuperscript{-1} which is very close to 10\textsuperscript{6} m s\textsuperscript{-1} in graphene. Their orbital-resolved electronic structure for MnX\textsubscript{3} show that the Dirac cone in majority spin channel consists of the d states of Mn and the P\textsubscript{z}, P\textsubscript{x} states of halogen. Particularly, The Dirac cone of MnI\textsubscript{3} almost completely consists of the P\textsubscript{z} and P\textsubscript{x} states of iodine. In contrast to graphene, which Dirac cone originates from the P\textsubscript{z} orbitals, the in-plane P\textsubscript{z} and P\textsubscript{x} orbitals of MnI\textsubscript{3} do not strongly interact with substrate. Therefore, the Dirac cone of MnI\textsubscript{3} is not easily affected by the supporting substrate.

Different from TM dihalides, TM trihalides consists of a honeycomb network of TM atoms similar to graphene (Figure 4b). The TM atoms are again connected through halogen atoms forming edge sharing octahedral. Zhang et al.\cite{93} found monolayer chromium trihalides CrX\textsubscript{3} (X=F, Cl, Br, I) are all ferromagnetic with out of plane anisotropy. According to Botana’s analysis,\cite{91} early TM halides tend to be antiferromagnetic because of the t\textsubscript{2g}–t\textsubscript{2g} AFM direct exchange. Since the TM–TM distance in TM trihalides is very close to that in TM dihalides,\cite{93} the t\textsubscript{2g}–t\textsubscript{2g} AFM direct exchange should be as strong as that in antiferromagnetic VCl\textsubscript{3}, VBr\textsubscript{2}, etc. The magnetic ground state of monolayer TiCl\textsubscript{3} is calculated to be ferromagnetic as well.\cite{96} The ferromagnetic ground state for these materials may be due to the strong localization of their 3d orbitals, as can be seen from the density of states plot in these studies.\cite{93,96} As the strong localization of 3d orbitals weakens the direct exchange interaction, the ferromagnetic superexchange interaction leads to ferromagnetism of TM trihalides. The experimentally realized monolayer CrI\textsubscript{3} is indeed ferromagnetic and has an out of plane easy axis.\cite{87} Bulk CrCl\textsubscript{3} is an A-type antiferromagnet whose spin lies in plane.\cite{100,106} In A-type antiferromagnets, the spin couple ferromagnetically within each layer and couple antiferromagnetically between adjacent layers. Many monolayer counterpart of bulk A-type antiferromagnets has been predicted to be ferromagnetic,\cite{93,107,108} which is a manifestation of weak interlayer vdW coupling. The evolution from easy-plane anisotropy for bulk A-type antiferromagnets to uniaxial out of plane anisotropy upon reduction to monolayer is often predicted, such as the case of CrCl\textsubscript{3}.\cite{93} Previously mentioned CoCl\textsubscript{2} and CoBr\textsubscript{2}.\cite{91} The uniaxial anisotropy again ensures the stabilization of inplane magnetic order down to monolayer. Ferromagnetism is found to be maintained in experimentally exfoliated few layer CrBr\textsubscript{2}.\cite{109} Note that although monolayer CrF\textsubscript{3} is found to be dynamically and thermally stable by first-principle calculation, bulk CrF\textsubscript{3} does not have vdW-type layered structure.

There exists a more complicate structure somewhere in between triangular lattice of TM dihalide and honeycomb lattice of trihalide. This peculiar M\textsubscript{3X}\textsubscript{8} structure is a deformed Kagome lattice in which the transition metal M cations form two triangles of different size.\cite{111} In many compounds, the small triangle [M\textsubscript{2}] is found to be a localized spin system owing to the metal–metal bonding.\cite{111,114} This results in a cluster-based triangular magnet similar to TM dihalides. More unusual physics can happen in M\textsubscript{3X}\textsubscript{8} system due to its complicate structure.(see the discussion about NbCl\textsubscript{3} in section 3).

Recently, some studies designed algorithm to computationally screen 2D magnetic materials from materials database.\cite{115-118} These algorithms focus on finding materials with layered structure and low exfoliation energy.\cite{116-119} The electronic and magnetic properties are then calculated by first principle. The paper by Torelli et al. emphasized the important role of spin wave gap on 2D magnetic material and they considered quantum correction to the magnetic anisotropy.\cite{115} These studies provide many candidates for 2D magnetic crystals although their prediction of magnetic properties for a single specific material may not be the most precise. The prediction of ferromagnetism in intrinsic electron-rich monolayer LaBr\textsubscript{3} may unveil new mechanism of ferromagnetism.\cite{120} There are still a lot of physics left for
2D magnetic system that can be studied using first principle technique.

### 3. Experimental Results for van der Waals Magnetic Systems

2D magnetic materials that have been experimentally demonstrated include the 2D form of the chromium compounds, Fe₅Ge₃Te₃ (FGT), sulfur phosphorus compound and some other materials like VSe₂, MnBiTe₃, and so on. Chromium compounds are one of the earlier reported materials. It mainly includes Cr₅Ge₃Te₅, CrI₃, and CrSiTe₃. These materials have been proven to be ferromagnetic atomic crystals. CrSiTe₃ shows obvious uniaxial anisotropy with a Curie temperature of 33 K.[134] In addition, it is predicted that the phase transition temperature of the single layer CrSiTe₃ will be higher than that of the bulk layer.[134] However, the phase transition temperature of Cr₅Ge₃Te₅ and CrI₃ layers is lower than that of multilayer. For example, the phase transition temperature of bilayer Cr₅Ge₃Te₅ is 30 K, bulk is 61 K.[88] And for CrI₃, the value of monolayer and bulk is 45 K and 61 K, respectively.[87] This is because the magnetic density of the material in 2D state is higher than that in 3D, and the excited state of 2D magnets at low temperatures will be stronger than that of 3D magnets. The original Cr₅Ge₃Te₅ thin layer is a 2D Heisenberg ferromagnet and its phase transition temperature is very sensitive to the applied low-intensity external magnetic field. Thus, it can be used as a ferromagnetic-paramagnetic transition material,[88] which is different from the properties of the bulk Cr₅Ge₃Te₅. Under pressure of more than 1 GPa, Cr₅Ge₃Te₅ can achieve the transformation from uniaxial anisotropy to planar anisotropy and its Curie temperature is also affected, decreasing from 66.6 to 60.6 K.[135, 136] The modulation of magnetic anisotropy by pressure control is relatively novel without applying any external magnetic field. CrI₃ shows an interesting magnetic phase associated with the number of layers, i.e., ferromagnetic in the odd number of layers, and antiferromagnetic in the even number of layers.[87] As the strength of the external magnetic field increases, the magnetic transition of the two-layer CrI₃ occurs, indicating that the antiferromagnetic coupling between the layers is relatively weak. Since the performance of the atomic thin layer material can be modulated by the gate voltage, the antiferromagnetic and ferromagnetic phases of the bilayer CrI₃ can be naturally controlled. This interesting interlayer phenomenon makes it possible to not only change the critical field of the magnetic transition, but also to foster an electrically controlled phase change.[132, 137] In addition, the spin direction of the antiferromagnetic state is determined by electrically modulating the relationship between the magnetization signals of the two antiferromagnetic states and the gate voltage under a zero magnetic field. This paves an unique pathway for the study of magnetoelectric control and spintronics of 2D atomic thickness magnetic materials. In addition to CrI₃, the magnetism of CrBr₃ and CrCl₂ has also been proven. Similar to CrI₃, magnetic tunnel junction composed of graphene/CrCl₂/graphene has been confirmed to reduce the antiferromagnetic order of CrCl₂ to bilayer.[138] Interestingly, the interlayers of CrCl₂ are antiferromagnetic, but the surface is ferromagnetic.

Ferromagnetic materials such as Fe₅Ge₃Te₃ (FGT) are used in modern storage devices due to their very large magnetic capabilities. In 2006, fewer layer of Fe₅Ge₃Te₃ was synthesized.[139] Theoretically, monolayer Fe₅Ge₃Te₃ can be obtained by the mechanical exfoliation method, of which the magnetostriuctive effect is obvious and the magnetostrictive energy can be therefore tuned by mechanical strain.[140] Experimentally, testing of the low temperature anomalous Hall effect has confirmed that the FGT is a metallic ferromagnetic body with an easy axial direction.[141] Having derived the monolayer FGT from the bulk using a Al₂O₃ assisted mechanical exfoliation method, an ion field effect transistor device is used to change the critical temperature and the coercive magnetic field of the fewer layer FGT. Tuning the gate voltage of FGT provides a method to improve the thin-layer phase transition temperature, through which the ferromagnetic behavior can be observed in room temperature.[142] Improvement of the Curie temperature of the FGT can also be achieved by patterning the FGT into a micron-scale microstructure with a focused ion beam, which results in a streak-to-vortex phase transition.[142] The dimensional effect is also greatly reflected in the FGT. The phase transition temperature and hysteresis loop of the fewer layer (3.2 nm) and the thick layer (48 nm) FGT are different. The magnetic domain of fewer layer FGT is characterized by a single magnetic domain and the thick FGT is represented by labyrinthine domain pattern, so the hysteresis loop changes from rectangular to mutant in a certain temperature range with increasing thickness from few layer to bulk.[143] Since ferromagnetism can be maintained in a monolayer FGT and the magnetic properties can be tuned by the electric field, it provides great possibilities for thin-layer FGT applications in magnetoelectric control and room temperature ferromagnetic research. Although the Curie temperature of some 2D ferromagnetic materials can be brought to room temperature by external modulation, it still has many difficulties in practical applications. Fortunately, few layer 1T-VSe₂ and single layer 1T-VSe₂ have been experimentally confirmed to be room temperature ferromagnets.[139, 144] It is reported that 1T-VSe₂ can be synthesized on a specific substrate, like HOPG (high temperature oriented pyrolytic graphite) and MoS₂, by molecular beam epitaxy.[139] A higher quality layer of material can also be obtained by using a formamide solvent to assist in the stripping of VSe₂, but monolayer exfoliated VSe₂ has not yet been reported.[145] Monolayer MnSe₂ grown on GaSe and SnSe₂ substrates also shows ferromagnetism at room temperature.[140]

There is a part of the sulfur phosphorus compound that is 2D antiferromagnetic material, such as Fe₅PS₃, FePSe₃, MnPS₃, and NiP₃S. It is difficult to control antiferromagnets by external magnetic fields due to their approximate zero net magnetization. However, they can store data information for applications of spintronics with high speed and low power owing to their robustness to charge and magnetic field disturbances. It is very difficult to directly measure the magnetic properties of antiferromagnets. But Raman spectroscopy provides a means for characterizing the magnetic order and properties of 2D materials with high quality. The characteristic peak of the polarized Raman spectrum of Fe₂S₃ was used as an indicator of antiferromagnetism, which demonstrated the Ising type antiferromagnetic order of thin Fe₂S₃ crystal with excellent structural stability. The phase transition temperature of Fe₂S₃ is about 115 K,
which is almost independent of the thickness from the bulk to the monolayer limit, indicating that the weak interlayer interaction has little influence on the antiferromagnetic order and antiferromagnetism can be maintained in a monolayer.\[89,147\] In fact, FePS\(_3\), FePSe\(_3\), MnPS\(_3\), and NiPS\(_3\) have the same structure and each of their layers is closely packed by two layers of S/Se atoms, and the metal ions and P2 pairs occupy octahedral vacancies.\[147\] Exerting a certain pressure on FePS\(_3\) and FePSe\(_3\) will cause the lattice in the plane to collapse and the phase transition from insulator to metal. FePSe\(_3\) has compressive superconductivity of low temperature and high pressure environment, but whether FePS\(_3\) has superconducting properties needs further study.\[148\] MnBi\(_2\)Te\(_4\), synthesized by the MBE method, showed an intrinsic antiferromagnetism according to low temperature magnetic measurements, while the in-plane coupling was ferromagnetic. The thickness of the film has a great influence on whether it is a quantum anomalous Hall insulator, making MnBi\(_2\)Te\(_4\) a potential material for studying the quantum anomalous Hall effect.\[149\]

Nb\(_3\)Cl\(_8\) is a van der Waals layered cluster magnet\[111\] (see discussion of MX\(_3\) structure in Section 2.5). Single-crystal Nb\(_3\)Cl\(_8\) made by the flux method using the solvent evaporation technique exhibits a magnetic-nonmagnetic phase transition at transition temperature 100 K.\[111\] The nonmagnetic phase transition originates from the structural transition at the same \(T_c\), accompanied by the interlayer charge transfer.\[111\] The interlayer charge transfer results in \([\text{Nb}]^{7+}\) and \([\text{Nb}]^{9+}\), which are paired spin states. The nonmagnetic phase transition does not happen in powder sample of Nb\(_3\)Cl\(_8\) because of the suppression of structural transition owing to the reduction of periodicity in powder sample.\[111\]

Although not in vdW layered structure, there are several thin film materials worth mentioned. For example, the thin film of intermetallic compound FeSn is antiferromagnetic with the Neel temperature of 370 K.\[150\] Co\(_3\)Sn\(_2\)S\(_2\) exhibits a second-order paramagnetic-ferromagnetic phase transition with \(T_c = 174\) K. The long range magnetic interaction is dominant in the Co\(_3\)Sn\(_2\)S\(_2\) by analysis of transition region by using Quantum Design MPMS (the magnetic property measurement system).\[151\]

### 4. Magnetism in vdW Heterostructure

Since the vdW materials have a naturally layered structure, we can use the van der Waals heterostructure constructed by individual single-layer material to explore new physics.\[155,166\] Due to the weak interlayer coupling, we can modify the crystal structure of multilayer vdW material through relative translation or rotation between layers. Sivadas et al. studied the magnetism of stacked bilayer Cr\(_1\) using first-principle calculations.\[167\] The calculated magnetic ground state showed that the magnetic order of bilayer Cr\(_1\) strongly depends on the stacking order. While the AB’ stacking (upper layer shift \(1/3 a_y + 1/3 a_y\) with respect to AA stacking) bilayer Cr\(_1\) is an A-type antiferromagnet, the AB-stacking (upper layer shift \(2/3 a_y + 1/3 a_y\) with respect to AA stacking) bilayer Cr\(_1\) is ferromagnetic.\[167\] The reason behind this stacking-dependent magnetism is the interlayer exchange interaction between Cr atoms is mediated through two iodine P orbitals, so called super-super-exchange (SSE) interactions.\[167\]

As we change the relative position of two Cr\(_1\) layers, the sign and strength of SSE between different (interlayer) Cr neighbors change accordingly\[97,98\] and the different competition between interlayer SSE interaction results in different magnetic order. It is worth mentioning that the AB’ stacking is corresponding to the high-temperature structure of bulk CrI\(_3\).\[168\] The nonmagnetic phase transition does not happen in powder sample.\[111\] Thenonmagneticphasetransitionoriginatesfromthestructuraltransitionatthesamespinstate.

Moreover, if we stack two single-layer material by deflecting a small relative angle, we can have regions of different local stacking order. This spatial variation of the stacking order is called the moire pattern. Combined with 2D materials exhibiting stacking-dependent magnetism we mentioned above, we can possibly engineer spatially dependent magnetic order through twisted bilayer system. In fact, the moire pattern itself can create complicated physics, as the well-known magic angle twisted bilayer graphene is found to exhibit a peculiar strongly correlated insulating state.\[170\] The strongly correlated state comes from the flattening of bands around Fermi level.\[171\] More interestingly, Sharpe et al. found an evidence of ferromagnetism in twisted bilayer graphene near 3/4 filling of the conduction band very recently.\[172\] They suggested that twisted bilayer graphene is a possible Chern insulator at 3/4 filling because of the observed large anomalous Hall effect in an insulating phase. Their nonlocal measurement also indicates the presence of chiral edge conduction. This surprising result tells us that the magnetism not only can be manipulated, but also can be possibly generated using vdW structures constructed by nonmagnetic 2D materials.

In 2017, Gong et al.\[173\] proposed a 2D antiferromagnetic half metal can be engineered by applying a vertical electric field across the plane of a bilayer A-type antiferromagnet, provided that the A-type antiferromagnet is an insulator or semiconductor. The idea utilizes the electronic structure of A-type AFM materials. Considering one layer of a bilayer A-type antiferromagnet, one spin component, say spin up electrons must have lower energy than spin down electrons because of the intralayer ferromagnetism. In the other layer, this order is reversed since the magnetic moments of two individual layers have to compensate each other (see Figure 1 in ref. [173]). Applying an out of plane electric field will shift bands of two constituent layers in opposite directions.\[173\] This opposite shifts will cause one spin component to close bandgap, while the other spin component become more insulating. Gong et al. chose the bilayer VS\(_2\) to demonstrate their idea.\[173\] The electronic structure by their density functional theory calculation indeed showed half metallic behavior. This opens another door for us to attain half metallicity in low dimensions.
and the large density of states at the Fermi level favors spin-zero. The magnetic structure emerges because the near-flat band at the Fermi level favors spontaneous magnetization according to Stoner’s criterion. Son et al. found the same magnetic structure in zigzag graphene nanoribbon by first-principle calculation. They showed that when spin polarization is included, the edge states around the Fermi level acquire a dispersion and a bandgap opens in the band structure of zigzag graphene nanoribbon (Figure 2 in ref. [175]). They further proposed that applying a transverse electric field can turn the zigzag graphene nanoribbon into a half metal owing to the opposite shifts of bands for two edges. The concept is similar to the electrically induced half metallicity in bilayer A-type magnet we discussed in the last section. Besides cutting 2D materials to create boundaries, it has been shown experimentally that large-area graphene samples will contain nanoboundaries. These inherent nanoboundaries can be considered as extended line defects in graphene. Line defects in graphene can cause spin accumulation and affect transport behaviors adjacent to the defect lines. Wu et al. observed a positive magnetoresistance when electron transports across the nanoboundary. Huang considered a 5–7 line defect model of graphene where hexagons are replaced by pentagons and heptagons in line defect. This structure is confirmed to be stable by ab initio calculation. By considering the Zee-man shift caused by external magnetic field and ripple induced Rashba spin–orbit coupling near the line defect, they calculated the magnetoresistance curve using the nonequilibrium Green’s function method (NEGF). The result fits the experimental data very well. It is evident that the presence of line defect structures will modify the magnetoresistance and related magnetic properties.

5. Induced Magnetism in Nonmagnetic 2D Materials

Since most of 2D materials are nonmagnetic, many efforts have been devoted to finding ways to induce magnetism in nonmagnetic 2D materials. One strategy is introducing boundaries by cutting 2D materials into quasi-1D nanoribbons. Zigzag-terminated graphene nanoribbon is known to have strongly localized states at the edges of the ribbon, which corresponds to the near-flat band at the Fermi level. Fujita et al. used the mean field approximation of Hubbard model to calculate the magnetic structure of zigzag graphene ribbon. They found one edge of the ribbon is spin up polarized, while the other edge is spin down polarized and the total magnetic moment of ribbon is zero. The magnetic structure emerges because the near-flat band and the large density of states at the Fermi level favors spontaneous magnetization according to Stoner’s criterion. Son et al. found the same magnetic structure in zigzag graphene nanoribbon by first-principle calculation. They showed that when spin polarization is included, the edge states around the Fermi level acquire a dispersion and a bandgap opens in the band structure of zigzag graphene nanoribbon (Figure 2 in ref. [175]). They further proposed that applying a transverse electric field can turn the zigzag graphene nanoribbon into a half metal owing to the opposite shifts of bands for two edges. The concept is similar to the electrically induced half metallicity in bilayer A-type magnet we discussed in the last section. Besides cutting 2D materials to create boundaries, it has been shown experimentally that large-area graphene samples will contain nanoboundaries. These inherent nanoboundaries can be considered as extended line defects in graphene. Line defects in graphene can cause spin accumulation and affect transport behaviors adjacent to the defect lines. Wu et al. observed a positive magnetoresistance when electron transports across the nanoboundary. Huang considered a 5–7 line defect model of graphene where hexagons are replaced by pentagons and heptagons in line defect. This structure is confirmed to be stable by ab initio calculation. By considering the Zee-man shift caused by external magnetic field and ripple induced Rashba spin–orbit coupling near the line defect, they calculated the magnetoresistance curve using the nonequilibrium Green’s function method (NEGF). The result fits the experimental data very well. It is evident that the presence of line defect structures will modify the magnetoresistance and related magnetic properties.

Apart from graphene, zigzag molybdenum disulfide (MoS₂) nanoribbon is found to be ferromagnetic by Li et al. Their first principle study showed that magnetism comes from the unsaturated Mo and S atoms at the edges. Different from zigzag graphene nanoribbon, the two edges of zigzag MoS₂ nanoribbon are ferromagnetically coupled. Zhou et al. predicted that zigzag gallium sulfide (GaS) nanoribbon is a half metal whose magnetic moment arises from Ga and S atoms at the Ga-terminated edge. The S-terminated edge does not contribute to magnetic moment. Because of the spin-polarized edge states, these zigzag nanoribbons are regarded as candidates for generating spin-polarized current, which is crucial for spintronic applications. Although MWH theorem prohibits long-range magnetic order in one dimension, several experimental works have already showed us that nanoscale edge magnetism is possible. It has been found experimentally that the
magnetic sequence in graphene nanoribbon can be modulated by controlling edge orientation and ribbon width even at room temperature.\cite{78} The interedge exchange interaction can also help to stabilize the magnetism.\cite{188} It should be noted that the electronic and magnetic properties of nanoribbon are sensitive to edge geometry as all three armchair nanoribbons of the above mentioned materials are nonmagnetic.\cite{175,184,185}

Periodic line defect in MoS$_2$ exhibits more interesting properties because of their large intrinsic spin–orbit coupling, 2H-phase MoS$_2$ is a well-known direct bandgap semiconductor. Two conduction band minimum and two valence band maximum of MoS$_2$ is located at two inequivalent k point, K and K’. These two special k points, called valleys, are direct consequence of the hexagonal crystal symmetry. Since space inversion symmetry is broken in MoS$_2$, the large intrinsic SOC of MoS$_2$ gives rise to the pronounced spin splitting in the valance band.\cite{189} Pulkin and Yazyev pointed out that the low energy hole transmission across an inversion boundary line defect is completely suppressed.\cite{190} Because of the time reversal symmetry, the highest valence band around K and K’ has different spin. Since the valley index will be swapped upon crossing a boundary between two opposite lattice orientation, the transport channel is prohibited by momentum and spin conservation.\cite{190} Obviously, this result is true only if the transport is in ballistic regime and there are no spin flip process attributed to ripple induced SOC near the line defect.

The opposite spin of the highest valance band locating at K and K’ is often called spin–valley coupling. This property can be utilized to create spin polarization. Valley-polarized transport is expected to take place in graphene containing 5-5-5 line defect\cite{191} (see Table 3). This is predicted by Gunlycke et al., stating that the degree of valley polarization of charge carriers transporting across 5-5-5 line defect depends on the incident angle between carriers and the direction parallel to defect.\cite{191} Pulkin et al. argued that this effect also occurs in MoS$_2$, line defect system.\cite{190} Different from graphene, the spin–valley coupling in MoS$_2$ renders charge carriers spin-polarized.\cite{190} If the carrier concentration is low enough, the spin polarization can be large and modulated by the incident angle.\cite{190} The spin polarization in line defect MoS$_2$ is confirmed by Pulkin and Yazyev using first-principles quantum transport calculation.\cite{190}

To create unpaired electron and local magnetic moment, another way is introducing vacancy defects in materials. For example, vacancy defects in graphene will induce localized states around the Fermi level, similar to the case of zigzag graphene nanoribbon.\cite{192} Yazyev and Helm showed that the localized states induced by vacancies lead to itinerant magnetism.\cite{193} They found that the states induced by vacancies in the same sublattice couple ferromagnetically while the states induced by vacancies in the different sublattice couple antiferromagnetically.\cite{193} The hydrocarbon chemisorption on graphene created by hydrogen plasma gives rise to the similar results\cite{193} because the motion of pi electrons of the absorbed states is quenched by the C–H bonding. As another example, monolayer NbSe$_2$ is predicted to be magnetic by introducing Nb vacancies whereas perfect monolayer NbSe$_2$ is nonmagnetic metallic.\cite{194} The reason is that the 4p orbitals of Se adjacent to the Nb vacancies produce large density of states at the Fermi level. Due to the two unpaired spin-up electrons occupying the $d_{xz}$ and $d_{yz}$ defect states, antisites W atom point defect can make monolayer WS$_2$ magnetic.\cite{195} Hole-doped semiconducting GaSe exhibit ferromagnetism and half metallicity because of the Mexican-hat like valence band near the Fermi level of pristine GaSe.\cite{196} Tuning the Fermi level via hole doping results in the van-Hove singularity at the Fermi level and exchange splitting. It can be seen that defect-induced magnetism strongly relies on Stoner-type mechanism.

In addition to theoretical calculations, experiments on defect-induced magnetism in 2D materials have also been reported. For instance, ultrathin metallic PtSe$_2$ is found to possess magnetism in the presence of Pt vacancies, and a 5% magnetoresistance is observed in the device on the application of a $\approx$25 mT magnetic field.\cite{197} Moreover, magnetism can be modulated by layer number of PtSe$_2$, due to the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange couplings across ultrathin films of PtSe$_2$.\cite{197} In another experiment, WS$_2$ with defects was obtained through annealing, and the magnetism at different annealing temperatures were confirmed by M–H loop.\cite{198}

Edges and vacancy defects in 2D materials are very reactive. The fact that they are easily contaminated by foreign gas molecules may weaken and destroy the defect induced magnetism.\cite{184} Moreover, it is hard to control the position and concentration of vacancy defects. Also there are other problems associated with point defects such as vacancies reconstruction and clustering of gas atoms.\cite{193,86} The introduction of magnetic impurities should be avoided during the material preparation, or the signal of the magnetism may come from the impurities in materials and the substrate.\cite{84} These issues hinder the experimental confirmation of defect induced magnetism, in fact debate on the defect induced magnetic order is not yet settled.\cite{199,86}

Since precise doping and defect engineering is hard, several studies proposed strain engineering as another method to induce magnetism without introducing defects.\cite{199,201} Applying strain will change the bond length, bond angle, wavefunction overlap of atoms, and thus the bond character. Strain engineering is suitable for 2D materials because they can sustain much larger elastic strain than bulk materials.\cite{202,203} Zhou et al.\cite{199} predicted that monolayer NbS$_2$ and NbSe$_2$ become ferromagnetic under 3% biaxial tensile strain, whereas compressed NbS$_2$ and NbSe$_2$ remain nonmagnetic. Applying stronger biaxial tensile strain can further stabilize the ferromagnetic ground state.\cite{199} They argued that reduced covalent interaction due to the increased bond length is the origin of this nonmagnetic to ferromagnetic transition. As an evidence, their first principle calculated density of states of unstrained NbS(Se)$_2$ showed that the self-exchange splitting of Nb 4d orbitals at the Fermi level is quenched by the hybridization between Nb 4d orbitals and S(Se) p orbitals.\cite{199} However, this unquenching of magnetism by applying tensile strain is not found in other transition metal dichalcogenides (TMDs) such as MoS$_2$, MoSe$_2$, and WSe$_2$ because they are semiconducting.\cite{199,204,206} Shi et al.\cite{200} found that hydrogenated monolayer MoS(Se)$_2$ can become ferromagnetic under 5% biaxial tensile strain. The n-type doping by adsorbed hydrogen atoms makes the electronic structure of MoS$_2$ similar to the NbS(Se)$_2$ one which has metallic character and states around the Fermi level mainly consisting of the 4d orbitals of transition metal atom.\cite{200} These results imply that simultaneous doping and strain engineering should be able to make TMDs become magnetic material. Experimentally, large strain can be applied by transferring 2D materials...
to a flexible substrate and then stretching the substrate.\cite{207,208} Nevertheless, the strain-induced magnetism is not yet observed experimentally.

Nonmagnetic 2D material can also be made magnetic by the proximity effect. Measurement of the Hall resistance reveals information about the magnetization of graphene coupling with yttrium iron garnet (YIG). The coexistence of magnetism and high carrier mobility of graphene is remarkable. At room temperature, there is an exchange field of about 0.2T between YIG and graphene, which can modulate the spin current in graphene by controlling the direction of the exchange field.\cite{51} Affected by spin-dependent interface scattering or ferromagnetic impurities, taking anomalous Hall effect as the only indicator of magnetic properties of materials is inappropriate. Therefore, in order to exclude the influence of magnetic impurities and various carriers on the anomalous Hall effect, the saturation magnetization of YIG is approximately the same as the magnetic field strength of the anomalous Hall resistance. It can be proved that the resistance of the anomalous Hall effect and the magnetization of graphene are related.\cite{209} Graphene can also be coupled with the ferromagnetic insulator EuS to increase the magnetic exchange field strength to 14T, or even larger.\cite{210} When EuS is coupled with monolayer WSe2, the magnetic exchange field generated between the interfaces can cause valley splitting of the single-layer WSe2, and the effective exchange field is up to 12T.\cite{211} If a heterostructure consisting of CrI3 and WSe2 is utilized, the magnetic exchange field can reach 13T and the control of the valley polarization and valley splitting of WSe2 can be achieved by controlling the magnetization of CrI3.\cite{51}

6. Prospects for 2D van der Waals Magnets

Through the previous chapter, we introduced the progress of 2D magnetic materials in recent years. The discovery of 2D magnetic materials including CrI3, Cr2Si2Te6, and VSe2 laid a solid foundation for the development of magnetic physics in 2D systems. As the family of 2D magnetic materials is rapidly growing, people begin to pay attention to them as a platform of magnetism to explore for basic physical problems and practical applications. We will discuss the future prospects of both antiferromagnetic and ferromagnetic 2D materials.

There are many kinds of antiferromagnetic 2D materials discovered at present, such as FePS3 and MnPS3. In recent years, the development of antiferromagnetic spintronics is gaining more and more attention.\cite{212} This is because antiferromagnetic materials have unique properties in many ways. For example, since antiferromagnetic materials do not exhibit macroscopic magnetic moment, they are not sensitive to external disturbances, thus making them highly stable. For another example, since the spin mechanical response of antiferromagnetic materials is in THz, it is superior to ferromagnetic materials in terms of fast information processing.\cite{213-215} In the past, the control of antiferromagnetic sequence is usually carried out by electricity. However, in the field of antiferromagnetic 2D materials, we can control the antiferromagnetic sequence of materials by regulating the crystal phase or the number of layers. For example, as mentioned in Section 3, CrI3 has a ferromagnetic order in a single layer, while a very peculiar antiferromagnetic state appears in a double layer, and several research groups have successfully regulated this antiferromagnetic state.\cite{53,87,216} In addition to CrI3, 2H-VSe2 is also predicted to exhibit this property of different magnetic sequences with different number of layers.\cite{217} Therefore, antiferromagnetic 2D materials can be widely used and developed in the construction of nonvolatile, high-density storage, and rapid information processing.

In addition to antiferromagnetic 2D materials, the other important aspect of 2D magnetism is the ferromagnetic 2D materials, represented by CrBr3 and Cr3Si, Te6. Ferromagnetic materials have always been the mainstream of modern magnetic research, and their applications in spintronics have been very mature. Corresponding spintronic devices, such as spin valves, magnetic sensors, magnetic tunneling junction, field effect transistor, current-driven magnetic flip devices, have also been widely studied and applied.\cite{218,219} Therefore, how to apply 2D magnetic materials to these fields has become an important direction of the development of 2D magnetic materials in the future.

At present, both antiferromagnetic 2D materials and ferromagnetic 2D materials have made some positive progress in applications of spintronics. The first research is about the performance of spin valve carried out on 2D magnetic materials. In 2015, the research of the vertical transport properties of Fe0.25TaS2/Fe0.25TaS2 vdW-magnetic tunnel junction(MTJ) was reported.\cite{220} In this MTJ, Fe0.25TaS2 serve as ferromagnetic (FM) layers, and the insulation layer between the magnetic layer is obtained by natural oxidation. Tunneling magnetoresistance (TMR) is about 6.5% at 5 K in this experiment. Fe3GeTe2 is then studied in another research group’s work, in which ultrathin hexagonal boron nitride (h-BN) is intercalated between two Fe3GeTe2 flakes.\cite{141} The TMR observed in this experiment is 160% at 4 K. Some other similar studies are applications of 2D magnetic materials to spin-filter magnetic tunnel junctions (sf-MTJs). These studies are mainly focused on CrX3(Y = I, Br, Cl).\cite{109,138,153,221,223} For instance, a bilayer CrCl3 is intercalated between two graphite flakes to construct a sf-MTJs, and a large magnetoresistance up to 106% is observed.\cite{138} A similar structure constructed with CrI3 instead of CrCl3 is measured by different research groups.\cite{153,221-223} The value of magnetoresistance measured in these experiments range from 550% to 1000000% due to the different experimental conditions. Moreover, the work to study tunneling through thin ferromagnetic CrBr3 barriers based on graphene–CrBr3–graphene sandwich structures is also reported.\cite{109} This work demonstrated that the spin polarized tunneling layers can be tunneled by magnetic emission rather than by phonons or localized states, as compared to nonmagnetic tunneling layers. In addition to the applications stated above, spin–orbit torque (SOT) device can be constructed with nonmagnetic layer interfaced with magnetic layer. Recently, the SOT devices based on 2D magnetic materials have been prepared.\cite{224,225} The researchers exfoliate Fe3GeTe2 (FGT) onto a substrate and sputtered a thin Pt film with several nanometers on the FGT. Then, the structure with FGT as the magnetic layer and Pt film as the nonmagnetic layer was obtained. When a small in-plane magnetic field is applied to the device, the out-plane magnetization of the device can be switched at a critical current. The heterostructure composed by nonmagnetic 2D material is also promising in the sense of practical applications, as Center for Advanced 2D Materials (CA2DM) in National University of Singapore has built a high sensitivity magnetic
Table 4. Magnetic orderings, phase transition temperature, acquisition method, and electrical properties of common vdW magnetic materials.

| Name                  | Magnetic orderings | Transition temperature | How to get                  | Electrical properties | Way of measurement                                      |
|-----------------------|--------------------|------------------------|------------------------------|-----------------------|----------------------------------------------------------|
| Cr$_2$Te$_5$ [87,88,135,152] | FM                 | $T_C = 68$ K (bulk), $T_C = 30$ K (bilayer) $T_C = 66.6 - 66$ K (under 0-1 GPa) | Exfoliation/synthesized by the flux method/MBE | Insulator       | Neutron powder diffraction Scanning magneto-optic Kerr microscopy |
| CrI$_3$ [53,137,153] | AFM (few layer; voltage controlling) FM (bulk, monolayer) | $T_C = 45$ K (monolayer), $T_C = 61$ K (bulk) | Exfoliation                     | Insulator       | Magneto-optical Kerr effect microscopy (MOKE) The magnetic circular dichroism (MCD) |
| CrCl$_3$ [128,138,154] | FM/AFM (interlayer) AFM (bulk) | $T_C = 17$ K (few layer) $T_C = 27$ K (bulk) | CVT/exfoliation                  | Insulator       | Vector network analyzer and physical properties measurement system (PPMS) |
| CrBr$_3$ [128,155] | FM                 | $T_C = 47$ K (bulk) | CVT                          | Insulator       | The magnetic circular dichroism (MCD) Torque magnetometer Magnetic balance |
| CrTe$_2$ [127,156] | FM                 | $T_C = 310$ K (bulk) | Metathesis in solution (K$_2$Te$_2$ and CrCl$_3$) | Semiconductor | Superconducting quantum interference device (SQUID) Quantum design (QD) magnetic property measurement system (PPMS) |
| CrSiTe$_3$ [134] | FM                 | $T_C = 170$ K (under stress) | Exfoliation                  | Insulator       | Anomalous Hall effect (AHE) measurement; Kondo effect measurement; Kerr rotation measurement (SQUID) X-ray magnetic circular dichroism (XMCD) Polar refractive magnetic circular dichroism (RMCD) |
| MnSe$_2$-1T [40] | FM (ultrathin layer); AFM (bulk) | $T_C = 300$ K (monolayer) | MBE                          | Metal           | SQUID |
| VS$_2$-1T [193] | FM (ultrathin layer) | $T_C = 300$ K (monolayer) | CVD/liquid exfoliation        | Semiconductor | SQUID PPMS |
| VS$_2$-1T [193] | FM (ultrathin layer) | $T_C = 300$ K (monolayer) | MBE/liquid-exfoliation (bulk to ultrathin) | Metal           | Longitudinal magneto-optic Kerr effect (L-MOKE) PPMS |
| MnBi$_3$Te$_4$ [50,149] | AFM (interlayer) /FM (surface) | $T_C = 30$ K (7 septuple-layer) | MBE                          | Insulator (QAH insulator or axion insulator) | SQUID |
| FePS$_3$ [89,147,162] | AFM                 | $T_N = 115–118$ K (monolayer) | CVT/exfoliation              | Insulator       | Raman Vibrating sample magnetometer (VSM) |
| NiPS$_3$ [147,163] | AFM                 | $T_N = 155$ K (bulk) $T_N = 130$ K (2L) | CVT                          | Insulator       | Raman; VSM; SQUID |
| MnPS$_3$ [147,164] | AFM                 | $T_N = 78$ K (bulk) | CVT                          | Insulator       | VSM; The neutron scattering |
| Nb$_2$Cl$_6$ [111] | AFM (powder) Paramagnetic (single crystal) | $T_N = 2$ K | The flux method using the solvent evaporation technique | Insulator       | The magnetic property measurement system (MPMS) |

CVT, chemical vapor transport; FM, ferromagnetism; AFM, antiferromagnetism; CVD, chemical vapor deposition; MBE, molecular beam epitaxy; QAH, quantum anomalous Hall.
sensor with low power consumption based on graphene/boron nitride bilayer.\cite{226}

In addition to the above application prospects, large-scale growth of magnetic 2D materials and the improvement of the critical temperature of magnetic semiconductors also need more long-term development and research. Currently, it is feasible to prepare magnetic 2D materials on a large scale by chemical vapor deposition (CVD). 2D materials including graphene and MoS$_2$ can be produced on a large scale by this method, and industries are already being built.\cite{227, 228, 229} Therefore, knowing how to use CVD method to improve the quality and yield magnetic 2D materials is one of the important directions for the development of magnetic 2D materials. The search for magnetic semiconductors with a critical temperature higher than room temperature is also one of the great expectations for 2D materials. At present, the critical temperature of 2D magnetic semiconductors is generally low, but some scholars have predicted that a few 2D magnetic materials have critical temperature above room temperature, such as 2-H phase monolayer VSe$_2$, monolayer Janus structure VS$_2$Se, etc.\cite{95, 125, 131, 136} Therefore, we have reasons to believe that room-temperature 2D magnetic semiconductors will be realized in the near future, and a major breakthrough in the development of the whole field of magnetism can be presumed.

7. Conclusions and Summary

2D magnetism have been an intriguing research for many decades since theory predicted that short-range interaction cannot sustain a long-range order in low dimensional magnetic systems. There are numerous studies, both theory and experiments, which investigate the possible origins of long range ordering in 2D system. Besides magnetization, polarization and other physical properties with possible long range order within a 2D system have also been intensively studied for its potential to push the Moore’s law limits in electronics. However, the MWH theorem is only valid under strict conditions, and thus spontaneous long range magnetic order is frequently observed in many physical systems. The naturally inherited atomic-layer cleavability and the magnetic anisotropy of 2D vdW magnets can possibly suppress spin fluctuations amidst short range interaction, providing an ideal platform to study magnetic phase transitions from bulk to 2D. Duality in electromagnetism is one of the most beautiful aspects of fundamental physics. Recently, the discovery of multiferroic materials reveals many interesting physical properties similar to magnetic materials, e.g., ferroelectricity is analogous to ferromagnetism. These phenomena raise an interesting issue: Does an electric version of MWH theorem exist? Consider the dipole–dipole interaction in low dimension, which is also a short range interaction in contrast to that in three dimension,\cite{231} an absence of polarization may be in order. Therefore, studies of low dimensional theorem in multiferroic system deserve further analysis.

Here we had reviewed the possibilities of spontaneous magnetization in 2D vdW magnetic systems. The magnetic properties of 2D vdW magnets are much more promising than their bulk counterpart for applications in various low power devices. The current characterization results for the magnetic properties of 2D vdW magnets are summarized in Table 4. Newly emerg-
The interaction energy of two dipoles separated by a displacement $r$ is $U \sim \frac{1}{r^3}[p_1 \cdot p_2 - 3(p_1 \cdot \hat{r})(p_2 \cdot \hat{r})]$. The radial part of space unit in integration $\int U \, d\mathbf{r} \text{ is proportional to } r^2 \text{ for } 3D \text{ and } r \text{ for } 2D$. Thus in 3D the integration is logarithmic divergence. In 2D, the integration behaves like $r^{-1}$ which is short range.