Magneto-optical and magneto-transport studies of 2D CrBr₃ and MnBi₂Te₄

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SINGAPORE

**MAGNETO-OPTICAL AND MAGNETO-TRANSPORT
STUDIES OF 2D CrBr_3 AND MnBi_2Te_4**

ZHAOWEI ZHANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2021

Magneto-optical and magneto-transport studies of 2D CrBr_3 and MnBi_2Te_4

ZHAOWEI ZHANG

SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as [Zhaowei Zhang, et al. "Direct photoluminescence probing of ferromagnetism in monolayer two-dimensional CrBr₃." Nano Letters 19.5 \(2019\): 3138-3142. DOI: 10.1021/acs.nanolett.9b00553](#)

The contributions of the co-authors are as follows:

- Prof. Gao and Prof. Yu conceived the experiment and supervised the project.
- Dr. Jiang, Dr. Shang and I performed the experiment.
- I wrote the manuscript with input from all authors.

Chapter 3 is published as [Chaolong Tang, Zhaowei Zhang, et al. "Magnetic proximity effect in graphene/CrBr₃ van der Waals heterostructures." Advanced Materials 32.16 \(2020\): 1908498. DOI: 10.1002/adma.201908498](#)

The contributions of the co-authors are as follows:

- Prof. Gao conceived the experiment and supervised the project.
- Dr. Tang, Dr. Lai, Dr. Tan and I performed the experiment.
- Dr. tang wrote the manuscript with input from all authors.

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ZHAOWEI ZHANG

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Abstract

Two-dimensional ferromagnetic materials show different properties compared with their bulk counterparts. The fundamental origins are reduced dimensionality and crystal symmetry. Atomically thin van der Waals ferromagnets have shown their advantages in highly tunable magnetism, uniform surface and flexibility. The realization of two-dimensional ferromagnetism not only inspires the study of fundamental physics, but also leads to new applications in spintronics and optoelectronics. Utilizing polarization resolved magneto-photoluminescence, we studied ferromagnetism in two-dimensional insulating CrBr_3 . We attributed the strong photoluminescence in CrBr_3 to the d-d transition. The Curie temperature of the monolayer is around 34 K, which is very close to that of the bulk. Ferromagnetic interlayer coupling is observed in layer-number dependent measurements. Our study on two-dimensional ferromagnetism in CrBr_3 has potential applications in van der Waals spintronics.

The magnetic proximity effect in two-dimensional graphene/ CrBr_3 heterostructures is observed. The Zeeman spin Hall effect probed by non-local measurements clearly indicates the strong magnetic proximity effect. The strength of the magnetic proximity effect is estimated by measuring Zeeman splitting field, which shows a significant magnetic proximity field even in a low magnetic field. More importantly,

the anomalous longitudinal resistance at the Dirac point $R_{XX,D}$ is dependent on the magnetic field near $\nu = 0$, which is ascribed to the magnetic proximity induced new ground state phases. The observation of the magnetic proximity effect in the graphene/CrBr₃ heterostructures reveals strong magnetic coupling between van der Waals materials and thus provides guidance for designing next-generation 2D spin logic and memory devices.

Nonreciprocal charge transport was observed in 5-SL MnBi₂Te₄. Though the crystal structure is inversion symmetric, the backscattering of charge carriers at the chiral edge is asymmetric, leading to directional magnetoresistance. We use the Al₂O₃ assisted method to fabricate MnBi₂Te₄ thin flakes. After estimating the thickness of obtained MnBi₂Te₄ thin flakes by optical contrast, the 5-SL sample is selected. The metal electrodes are then fabricated by a stencil mask. The quantum anomalous Hall effect at high magnetic field is demonstrated, which confirmed the chiral edge channel. The second order magnetoresistance is used to study the nonreciprocal charge transport and dependence on the magnetic field shows clear hysteresis loops due to the finite net magnetic moment at zero magnetic field. The chirality of the hysteresis loop is tuned by applying the gate voltages, which results from the difference in scattering rate between electrons and holes. The study of nonreciprocal charge transport paves the way to develop new electronic devices using magnetic topological van der Waals materials.

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Chapter 1

Introduction

The history of magnetism is coeval with the history of human society. Over two millenia, people have been interested in the rich phenomena relevant to magnetic materials. For example, the magnet attracts objects acting at a distance. Not only the interesting behaviours of magnets captivated countless curious spirits, but also the application of magnets greatly improves the human's life. The south pointer turns on the base to align it's handle with the earth's magnetic field, which is used to resolve directions in early days. More recently, magnetic materials are used to built electronic devices for computing, sensing and memory. Though there is a long history of using magnetic materials, the knowledge of magnetism developed relatively slowly, until the discovery of the quantum mechanism. After that, the quantum nature of the magnetism has been revealed.

Magnetic materials are widely used in spintronic devices. In 2007, Nobel Prize for Physics went to Professors Peter Grünberg and Albert Fert for the discovery

of giant magnetoresistance (GMR), where the spin as well as the charge of the electron is manipulated and exploited in magnetic materials. The spin degree of freedom of the charge in magnetic materials has shown excellent properties as information carrier, such as high speed, non-volatile and low power consumption. New magnetic materials, such as two-dimensional van der Waals magnetic materials have attracted lots of interests in physics and material communities. These new materials provide a platform to study the fundamental physics in magnetism and devices with high performance.

1.1 Quantum nature of magnetism

1.1.1 Exchange interaction

The characteristic feature of a ferromagnet is its spontaneous magnetization. Pierre Weiss proposed the first modern theory of ferromagnetism in 1906. He pointed that there is an internal ‘molecular field’ $\mathcal{H}_{inter}$, which is proportional to the magnetization. Heisenberg pointed out the origin of $\mathcal{H}_{inter}$ is exchange interaction. The Pauli principle forbids two electrons to occupy the same quantum state. For two electrons at site i and j , exchanges of them give the same electron density:

$$|\Psi(i, j)|^2 = |\Psi(j, i)|^2, \quad (1.1)$$

where $\Psi(i, j)$ is the product of space function $\psi(i, j)$ and spin coordinates $\chi(i, j)$. Meanwhile, the fermionic nature of electrons acquires the total function to be

antisymmetric:

$$\Psi(i, j) = -\Psi(j, i). \quad (1.2)$$

Taking hydrogen molecule as an example. Neglecting the interaction between electrons, Schrödinger's equation can be written as:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial r_j^2} \right) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_i} + \frac{1}{r_j} \right) \right] \Psi(r_i, r_j) = \varepsilon \Psi(r_i, r_j), \quad (1.3)$$

where $\hbar$ is the reduced Planck constant, m is the mass of the electron, e is the elementary charge, ϵ_0 is the vacuum dielectric constant, and ε is the energy of the system. Two molecular orbitals, a bonding orbital ϕ_s and an antibonding orbital ϕ_a are written as:

$$\phi_s = \frac{1}{\sqrt{2}}(\psi_i + \psi_j) \quad \phi_a = \frac{1}{\sqrt{2}}(\psi_i - \psi_j), \quad (1.4)$$

where ψ_i and ψ_j are spatial components of the wave function of two electrons, respectively. For the spin triplet state $\mathbf{S} = 1$, the spin function is symmetric:

$$\chi_s = |\uparrow_i, \uparrow_j\rangle; \quad \frac{1}{\sqrt{2}}(|\uparrow_i, \downarrow_j\rangle + |\downarrow_i, \uparrow_j\rangle); \quad |\downarrow_i, \downarrow_j\rangle, \quad (1.5)$$

where $|\uparrow\rangle$ and $|\downarrow\rangle$ represent spin-up and spin-down state, respectively. For the spin singlet state $\mathbf{S} = 0$, the spin function is antisymmetric:

$$\chi_a = \frac{1}{\sqrt{2}}(|\uparrow_i, \downarrow_j\rangle - |\downarrow_i, \uparrow_j\rangle). \quad (1.6)$$

We rewrite the total wave function of the system:

$$\Psi_{singlet} = \phi_s \chi_a \quad \Psi_{triplet} = \phi_a \chi_s, \quad (1.7)$$

where $\Psi_{singlet}$ and $\Psi_{triplet}$ are total wave function of the spin singlet state and spin triplet state. The energy of two states can be evaluated as:

$$\begin{aligned} \varepsilon_{singlet} &= \int \Psi_{singlet}^* \mathcal{H} \Psi_{singlet} \\ &= \int \phi_a^* \chi_s^* \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial r_j^2} \right) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_i} + \frac{1}{r_j} \right) \right] \phi_a \chi_s d^3r_i d^3r_j \end{aligned} \quad (1.8)$$

$$\begin{aligned} \varepsilon_{triplet} &= \int \Psi_{triplet}^* \mathcal{H} \Psi_{triplet} \\ &= \int \phi_s^* \chi_a^* \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial r_j^2} \right) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_i} + \frac{1}{r_j} \right) \right] \phi_s \chi_a d^3r_i d^3r_j. \end{aligned} \quad (1.9)$$

There is the energy difference between spin singlet and spin triplet state:

$$\begin{aligned} \varepsilon_{singlet} - \varepsilon_{triplet} &= 2\mathcal{J} \\ &= \int \psi_i^*(r') \psi_j^*(r) \mathcal{H} \psi_i(r) \psi_j(r') d^3r d^3r' \end{aligned} \quad (1.10)$$

We can rewrite the energy of the system using the exchange integral $\mathcal{J}$ as:

$$\varepsilon = -2 \left(\frac{\mathcal{J}}{\hbar} \right) \mathbf{s}_i \cdot \mathbf{s}_j. \quad (1.11)$$

And the exchange Hamiltonian has the form:

$$\mathcal{H}_{ex} = -2\mathcal{J} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad (1.12)$$

where $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are the dimensionless spin operator. The nature of the exchange interaction is the Coulomb interaction between electrons. It determines whether the system prefers a parallel spin configuration or an antiparallel spin configuration. When $\mathcal{J} > 0$, the parallel spin configuration is the low-energy state and the system prefers ferromagnetic coupling. When $\mathcal{J} < 0$, the antiparallel spin configuration is the low-energy state and the system prefers antiferromagnetic coupling.

1.1.2 Spin-orbit interaction

In solid state systems, spin-orbit interaction plays an important role by adding a spin-dependent term in Hamiltonian and lifting the degeneracy of the spin-up band and spin-down band. It arises from the interacting with the effective magnetic field produced by the rotating electrons. By adding the spin-orbit term, the Hamiltonian can describe the physics in a more accurate way. Now we consider the simplest situation where the electron rotates around the nucleus with proton number Z . The spin-dependent term in the Hamiltonian has the form:

$$\mathcal{H}_{SO} = -\gamma \hat{\mathbf{S}} \cdot \hat{\mathbf{B}}, \quad (1.13)$$

where γ is the gyromagnetic ratio of the electron, $\hat{\mathbf{S}}$ is the spin operator and the $\hat{\mathbf{B}}$ is the effective magnetic field seen by the electron. The effective magnetic field $\mathbf{B}$ is given by:

$$\mathbf{B} = -\frac{\vec{v} \times \mathbf{E}}{2c^2}, \quad (1.14)$$

where $\vec{v}$ is the velocity of the electron, and $\mathbf{E}$ is the electric field. The electric field is given by:

$$\begin{aligned}\mathbf{E} &= -\nabla\phi(\mathbf{r}) \\ &= -\nabla\left(\frac{Ze^2}{4\pi\epsilon_0 r}\right) \\ &= \frac{Ze^2}{4\pi\epsilon_0 r^3}\mathbf{r}\end{aligned}\tag{1.15}$$

where ϕ is the scalar potential. Then we can rewrite the spin-orbit Hamiltonian as:

$$\begin{aligned}\mathcal{H}_{SO} &= \frac{e}{2m}\hat{\mathbf{S}} \cdot \left(-\frac{\hat{\mathbf{p}}}{m} \times \frac{Ze^2}{16\pi\epsilon_0 r^3}\hat{r}\right) \\ &= \frac{Ze^3}{16m\pi\epsilon_0 r^3}\hat{\mathbf{S}} \cdot \hat{\mathbf{L}},\end{aligned}\tag{1.16}$$

where $\hat{\mathbf{L}}$ is the angular momentum. The above discussion indicates that the spin-orbit interaction is usually stronger in the system with larger proton numbers.

The spin-orbit interaction term in solid can be forbidden if time reversal symmetry and crystal inversion symmetry are conserved. When the system has time reversal symmetry, at any position of the Brillouin zone, it must obey:

$$\varepsilon(k, \uparrow) = \varepsilon(-k, \downarrow),\tag{1.17}$$

where ε is the energy, k is the wave vector, $\uparrow$ and $\downarrow$ represent spin-up and spin-down state, respectively. If the system also has crystal inversion symmetry, the system also obeys:

$$\varepsilon(k, \uparrow) = \varepsilon(-k, \uparrow).\tag{1.18}$$

Therefore, for systems with both time-reversal symmetry and inversion symmetry, each electronic state is spin-degenerate:

$$\varepsilon(k, \uparrow) = \varepsilon(k, \downarrow), \quad (1.19)$$

Overall, spin-orbit interaction is very important in solid state system. For example, in monolayer transition metal dichalcogenides MoS_2 , MoSe_2 , WS_2 and WSe_2 , crystal inversion symmetry is broken. The spin-orbit interaction lift the degeneracy of the spin-up and spin-down band, resulting in the spin-valley locking. Based on the spin-valley physics, lots of vallytronic devices are designed, such as valley transistors, which paves ways to low-power memory and logic device applications.

1.1.3 Crystal field interaction

In compounds, magnetic ions are not isolated, but interacting with surrounding ions (ligands). A simplified way to describe the interaction is to treat the surrounding ions as negative point charges. The crystal field theory describes the effect of the local electric environment on the energy level of the magnetic atom/ion, whose nature is the Coulomb interaction. Therefore, the size of the crystal field is closely related to the symmetry of the local environment. Taking d-orbital electrons of an ion as an example, the angular distribution is shown in Figure 1.1a. When the ion is placed in the lattice as shown in Figure 1b, the local electric environments are usually not spherically symmetric. Therefore, electrostatic repulsion of different orbitals varies. In the octahedral lattice, the electrostatic repulsion of $d_{x^2-y^2}$ is

FIGURE 1.1: An example of crystal field lifting the 5-fold degeneracy of d orbitals. (a) Distribution of d-orbital electrons shows angular dependence. (b) A magnetic atom/ion in the octahedral lattice. (c) (d) d_{xy} and $d_{x^2-y^2}$ orbital in an octahedral lattice. d_{xy} is lowered in energy with respect to $d_{x^2-y^2}$ orbital. (e) Without considering the crystal field, the d orbitals of the magnetic atom/ion are degenerate. The crystal field arising from electrostatic repulsion, lifts the degeneracy of d orbitals.

larger than that of d_{xy} orbital, as shown in Figure 1.1 c and d, where the crystal field is produced by p orbitals. Therefore d_{xy} is lowered in energy with respect to $d_{x^2-y^2}$ orbital. As shown in the left part of Figure 1.1e, without considering the crystal field, the d orbitals are degenerate. The crystal field arising from electrostatic repulsion, lifts the degeneracy of d orbitals as shown in the right part of the Figure 1.1 e. Electrons will first occupy the low energy band. Based on this

understanding, the crystal field is written as:

$$\mathcal{H}_{cf} = \int \rho(\mathbf{r})\phi(\mathbf{r})d^3\mathbf{r}, \quad (1.20)$$

where $\rho(\mathbf{r})$ is the charge density and $\phi(\mathbf{r})$ is the potential of the crystal environment. The effect of the crystal field on the magnetic ions depends on the symmetry of the lattice. For instance, the crystal field of pentagonal bipyramidal lattice and square antiprismatic lattice are shown in Figure 1.2.

FIGURE 1.2: Crystal field of pentagonal bipyramidal lattice and square antiprismatic lattice.

1.1.4 Spin wave theory

A ferromagnet is perfectly spin ordered when the temperature is 0 K. At a finite temperature, however, the cost of energy for a weak distortion of a ground state configuration almost vanishes. The long wavelength of the spin distortion is the spin waves, quantized as magnons. For a one-dimensional spin chain with ground

state $|\Psi\rangle$, all spins are lying along the $+z$ direction. In this case, the Hamiltonian for the Heisenberg model can be written as:

$$\hat{\mathcal{H}} = -2J \sum_i [\hat{\mathbf{S}}_i^z \hat{\mathbf{S}}_{i+1}^z + \frac{1}{2}(\hat{\mathbf{S}}_i^+ \hat{\mathbf{S}}_{i+1}^- + \hat{\mathbf{S}}_i^- \hat{\mathbf{S}}_{i+1}^+)], \quad (1.21)$$

and

$$\hat{\mathcal{H}}|\Psi\rangle = -NS^2J|\Psi\rangle \quad (1.22)$$

To create a magnon, we flip a spin at site j . The state $|j\rangle$ can be written as:

$$|j\rangle = \hat{\mathbf{S}}_j^- \hat{\Psi} \quad (1.23)$$

Applying the Hamiltonian to state $|j\rangle$, we get

$$\hat{\mathcal{H}}|j\rangle = 2[(-NS^2J + 2SJ)|j\rangle - SJ|j+1\rangle - SJ|j-1\rangle]. \quad (1.24)$$

But, this state is not the eigenstate of the Hamiltonian. We need to diagonalize the Hamiltonian. To this end, we can look for plane wave solutions as the form:

$$|q\rangle = \frac{1}{\sqrt{N}} \sum_j e^{iqR_j} |j\rangle. \quad (1.25)$$

Then, we have

$$\hat{\mathcal{H}}\hat{q} = E(q)\hat{q}, \quad (1.26)$$

where $E(q)$ is the energy and is written as:

$$E(q) = -2NS^2J + 4JS[1 - \cos(qa)]. \quad (1.27)$$

Therefore, the energy of magnon excitation is

$$\hbar\omega = 4JS[1 - \cos(qa)]. \quad (1.28)$$

Above discussion shows that flipping a spin of the system changes the total spin by $\frac{1}{2} - (-\frac{1}{2}) = 1$. So, magnons are bosons with spin angular momentum of $-\hbar$. Then, we will show the excitation of magnons will reduce the total magnetization. At a low temperature, only small q and small ω are important. At small q , we have

$$\hbar\omega \approx 2JSq^2a^2. \quad (1.29)$$

The density of states in three dimensions is given by

$$g(\omega) = \left(\frac{1}{2\pi}\right)^3 4\pi q^2 \frac{dq}{d\omega}. \quad (1.30)$$

where $\omega(q)$ is the dispersion of magnons, which is given by Equation (1.29). So, we will have:

$$\frac{d\omega}{dq} = \frac{4JSqa^2}{\hbar}. \quad (1.31)$$

Therefore, the density of states of magnons can be written as:

$$g(\omega) = \frac{1}{4\pi^2} \left(\frac{\hbar}{2JSa^2} \right)^{\frac{3}{2}} \sqrt{\omega} \quad (1.32)$$

The number of magnon modes at temperature T can be obtained by integrating the magnon density of state over all frequencies after multiplying by the Bose factor:

$$\begin{aligned} n_{magnon} &= \int_0^\infty \frac{g(\omega) d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \\ &= \frac{1}{4\pi^2} \left(\frac{\hbar}{2JSa^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\omega} d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \\ &\propto T^{\frac{3}{2}} \end{aligned} \quad (1.33)$$

At temperature $T = 0K$, all magnetic moments are aligned at the same direction with magnetization of $M(0)$. At the temperature T , the number of thermally excited magnons is proportional to $T^{3/2}$. Each thermally excited magnon mode reduces the total magnetization by $S = 1$. In this case, the reduced magnetization $\Delta M(T) = M(T) - M(0)$, is proportional to $M(0)T^{3/2}$. Therefore, the magnetization at the temperature T is $M(T) \propto M(0) - M(0)T^{3/2}$. This result shows the magnetization reduces as a function of temperature. Noting that this result is only valid in three dimensions and at a low temperature range.

1.2 Hall effect

When a bunch of electrons or holes are restricted in two dimensions, applying external magnetic field leads to rich and beautiful behaviours. Due to the Lorentz

force acting on the charge, the charge current J_x flowing in the x direction of a sheet of material is deflected and bends towards the y direction. To cancel the bending of the charge current, an electric field E_y is developed, so called Hall effect. Edwin Hall discovered the Hall effect in 1879. At low temperature and under a high magnetic field, the Hall resistance R_{xy} becomes quantized as $\frac{h}{e^2} \frac{1}{\nu}$, where ν is an integer. This is known as quantum Hall effect. It's also found that ν is not only restricted to be an integer, but it can take fractions, which is known as fraction quantum Hall effect. Remarkably, these behaviours arise from important physics and become a platform to study spin-orbit interaction, chiral edge states and band topology.

1.2.1 Classic Hall effect

Arising from the motion of charge carrier in the magnetic field, classical Hall effect is illustrated in Figure 1.3. To describe the classic Hall effect, we first consider the motion of electrons in the magnetic field:

$$m \frac{d\mathbf{v}}{dt} = -e\mathbf{v} \times \mathbf{B}, \quad (1.34)$$

where m is the mass, $\mathbf{v}$ is the velocity, t is the time, e is the elementary charge and $\mathbf{B}$ is the magnetic field. Solving this equation, we get:

$$X = X_0 - R \sin(\omega_B t + \phi), Y = Y_0 + R \cos(\omega_B t + \phi), \quad (1.35)$$

where cyclotron frequency $\omega_B = \frac{eB}{m}$.

Next, we talked about Drude model, which describes the motion of electrons in electric field $\mathbf{E}$ and magnetic field $\mathbf{B}$. The equation of the motion is:

$$m \frac{d\mathbf{v}}{dt} = -e\mathbf{E} - e\mathbf{v} \times \mathbf{B} - m \frac{\mathbf{v}}{\tau}, \quad (1.36)$$

where τ is the scattering time corresponding to the average time between collisions. The third term in Equation (1.36) arises from electron bouncing off. The origin of this collision in material could be defect, phonon, or other electrons. When the V_H develops and thereby cancels the cyclotron motion, we have $\frac{d\mathbf{v}}{dt} = 0$. We note that the current J_x relates to the velocity v by $J_x = -nev$, where n is the electron density. The Equation (1.36) can be written as:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{ne} \begin{bmatrix} \frac{m}{e\tau} & B_z \\ -B_z & \frac{m}{e\tau} \end{bmatrix} J_x \quad (1.37)$$

The above equation has the same form as Ohm's law: $\mathbf{E} = \rho J_x$, where the resistivity ρ is a two by two tensor. The Hall resistivity ρ_{xy} scales linearly with the magnetic field by:

$$\rho_{xy} = \frac{B_z}{ne}. \quad (1.38)$$

FIGURE 1.3: Classic Hall effect

1.2.2 Quantum Hall effect

Another milestone in the study of Hall effect is the discovery of the quantum Hall effect in 1980[23]. Under strong out-of-plane magnetic field, the Hall resistance shows a series of plateaux labeled by integer ν . At these plateaux, the Hall resistance takes exactly quantized value

$$R_{xy} = \frac{h}{\nu e^2}, \quad (1.39)$$

where h is the Planck's constant, e is the elementary charge and ν is the filling factor of the Landau level, while value of the magnetoresistance takes zero. Quantum Hall effect arises from the combined effects of Landau level, edge states and disorder, where classic description does not work.

Landau Level

When charged particles moving in two dimensions are subject to the out-of-plane magnetic field, the Hamiltonian of the system is described as:

$$\mathcal{H} = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 + \mathbf{V}(\mathbf{z}) \quad (1.40)$$

Taking the Landau gauge $\mathbf{A} = (0, Bx, 0)$. To solving the Schrödinger equation:

$$\mathcal{H}\phi(x, y, z) = \epsilon\phi(x, y, z), \quad (1.41)$$

we separate the total energy into two parts $\epsilon = \epsilon_z + \epsilon_{xy}$. We take the Landau gauge, where $\mathbf{A} = xB\hat{y}$. We consider the movement of electrons in xy plane and ignore

the movement in z axis. Since $\mathbf{A}$ is independent on y , the solution of the equation should have the form as $\phi_{xy} = u(x)e^{ixy}$. Therefore, the Schrödinger equation can be simplified as:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_L^2(x + l_B^2 k)\right]u(x) = \epsilon_{xy}u(x), \quad (1.42)$$

where $\omega_L = \frac{eB}{m}$ is the cyclotron frequency and $l_B^2 = \frac{\hbar}{eB}$ is the magnetic length. The energy is:

$$\epsilon_{xy} = \epsilon_n = \hbar\omega_L\left(n - \frac{1}{2}\right), n = 1, 2, 3... \quad (1.43)$$

Under strong magnetic field, the Landau levels are developed and the degeneracy is lifted, which is a key ingredient for us to understand the quantum Hall effect.

Edge States

Classically, electrons moves in cycles under strong magnetic field. When all electrons motion is anti-clockwise, motions of electrons at the left edge and the right edge are different. For the left edge, when electrons collide with the boundary, the only path for electrons to move is to bounce back and keep moving in one single direction owing to the strong magnetic field. The left edge and right edge therefore have opposite moving directions, which is called opposite chirality.

In a quantum picture, the electrons moving in the sample are subjected in a potential $V(x)$. Here the length of the sample is considered as infinite. The Hamiltonian therefore is:

$$\mathcal{H} = \frac{1}{2m}(p_x^2 + (p_y + eBx)^2) + V(x) \quad (1.44)$$

Suppose the potential $V(x)$ evolves smoothly in the range of the magnetic length l_B , it can be Taylor expanded around the location X :

$$V(x) = V(X) + \frac{\partial V(x)}{\partial x}(x - X) + \dots \quad (1.45)$$

We only keep the linear potential that gives rise to the drift velocity in y direction:

$$v_y = -\frac{1}{eB} \frac{\partial V(x)}{\partial x} \quad (1.46)$$

Edge states show different behaviours compared to the bulk. When the Fermi level is not located at the Landau level, the bulk states are unoccupied while edge states are occupied. In other words, the bulk shows insulating behaviours while edge exhibits conductive behaviours. With this approximation, we can calculate the current flowing in the sample:

$$I_y = -e \int \frac{dk}{2\pi} v_y(k) = \frac{e}{2\pi l_B^2} \int dx \frac{1}{eB} \frac{\partial V}{\partial x} = \frac{e}{2\pi\hbar} \Delta \mu \quad (1.47)$$

The Hall conductivity $\sigma_{xy} = \frac{I_y}{V_H} = \frac{eI_y}{\Delta\mu}$ therefore is:

$$\sigma_{xy} = \frac{e^2}{2\pi\hbar} \quad (1.48)$$

The Hall conductivity shown above represents the contribution of a single conducting channel. It turns out that the Hall conductivity is quite robust. The integral is independent to the shape of potential $V(x)$. Meanwhile, the backscattering requires electrons to be scattered to the other edge of the sample, which is highly

suppressed. The chiral nature of the edge state forces the electron motion in one direction without backscattering.

1.2.3 Quantum anomalous Hall effect

The quantum Hall effect without magnetic field is called quantum anomalous Hall effect[24]. A simple physical picture of the quantum anomalous Hall effect is described as follows.

At zero temperature, the Hall conductance can be described by the Kubo formula:

$$\sigma_H = \frac{e^2}{h} \frac{1}{2\pi} \int d^2k (\partial_{k_x} a_y - \partial_{k_y} a_x), \quad (1.49)$$

where

$$a_{x(y)} = -i \sum_{n=1}^M \langle nk | \frac{\partial}{\partial k_{x(y)}} | nk \rangle. \quad (1.50)$$

The formula describes the band insulator with M of N bands are occupied. $a = (a_x, a_y)$ is the gauge field in momentum space that describes the Berry's phase. The flux on the Brillouin zone torus is always quantized, which is called the first Chern number. Under a strong magnetic field, the degeneracy of Landau levels is lifted and the edge channels are developed, where the quantized Hall resistance is observed in the quantum Hall effect. Without the magnetic field, Haldane developed the first model with quantized Hall resistance in a honeycomb lattice in Figure 1.4. Apart from the nearest-neighbour hopping term between A and B sublattices, the complex second-neighbour hopping term is also included. The Hamiltonian of this

model is:

$$\begin{aligned}
 H(\mathbf{k}) = & 2t_2 \cos \phi \left(\sum_i \cos(\mathbf{k} \cdot \mathbf{b}_i) \right) \mathbf{I} \\
 & + t_1 \left[\sum_i [\cos(\mathbf{k} \cdot \mathbf{a}_i) \sigma_1] + \sin(\mathbf{k} \cdot \mathbf{a}_i) \sigma_2 \right] \\
 & + [M - 2t_2 \sin \phi \sum_i \sin(\mathbf{k} \cdot \mathbf{b}_i) \sigma_3],
 \end{aligned} \tag{1.51}$$

where σ_i is the Pauli matrices for A and B sublattices, t_1 is the nearest-neighbour hopping, t_2 is the complex second-neighbour hopping, ϕ is the phase accumulated by the t_2 hopping and M is the on-site energy. As shown in Figure 1.4b, when taking the phase ϕ into account, the gaped system with finite mass host the quantized Hall conductivity $\sigma_{xy} = \frac{\nu e^2}{h}$. In this case, the quantum anomalous Hall effect is realized.

FIGURE 1.4: Haldane model for quantum anomalous Hall effect. (a) The honeycomb lattice with complex next-nearest-neighbor hopping. (b) The phase diagram of the Haldan model where the Hall conductivity is $\sigma_{xy} = \frac{\nu e^2}{h}$. Adapted from Reference [1] with permission.

1.3 Magnetism in two-dimensions

1.3.1 Mermin-Wagner theorem and ferromagnetism in the monolayer

The reduced dimensionality in two-dimensional materials leads to new physics and potential applications in the area of electronics, spintronics and optoelectronics. As an important part of two-dimensional materials, two-dimensional ferromagnetic materials were first reported in 2017. Xu group and Zhang group reported their experimental discovery of two-dimensional ferromagnets independently[2, 3]. For example, Figure 1.6 shows ferromagnetism in monolayer CrI_3 . The other reported material is insulating $\text{Cr}_2\text{Ge}_2\text{Te}_6$ that obtained by mechanical exfoliation. After that, other materials with different magnetic properties are reported, such as metallic Fe_3GeTe_2 and CrTe_2 [6, 25]. Layered magnetic materials have shown their advantages: high tunability, high flexibility, and atomically flat interface. Based on these properties, a bunch of spintronic devices built by two dimensional magnetic materials have been demonstrated, including spin valves and spin transistors. The study of two-dimensional magnetic materials paves ways to high-performance, low-consumption devices for memory and computing.

Ferromagnetism in three-dimensional materials has been widely studied. When it comes to two dimensions, Mermin-Wagner theorem predicted long-range spin order is prohibited in isotropic Heisenberg model unless the system is at $0K$ [26].

FIGURE 1.5: Ferromagnetism in the monolayer limit. (a) Ferromagnetic hysteresis loops of the magneto-optical Kerr effect in monolayer CrI₃. (b) Temperature dependent Kerr rotation in monolayer CrI₃. Adapted from Reference [2] with permission.

Magnetic anisotropy, however, overcomes this restriction and protected the ferromagnetism at the finite temperature.

FIGURE 1.6: Spin-wave excitation in two dimensions and three dimensions. (a) and (b) shows the spin wave excitation in two dimensions and three dimensions. In the monolayer limit, the intralayer exchange interaction plays the key role. (c), (d) and (e) shows the magnon density of states in monolayer, multilayer and bulk materials. Adapted from Reference [3] with permission.

As shown in Figure 1.6, the magnon excitation in two dimensions is different from

that in three dimensions[27]. As shown in Figure 1.6c, in monolayer, the density of states $g_{2D}(\omega)$ is a constant C . Putting this density of states into equation (1.51), we find the integral diverges. This indicates a gapless energy dispersion relation of magnons, and very small thermal fluctuation will destroy the long range spin order in isotropic two-dimensional systems. The magnetic anisotropy, however, opens a magnon excitation gap through the energy difference between in-plane magnetic orders and out-of-plane magnetic orders. This energy difference stabilizes the ferromagnetism in two dimensions.

1.3.2 Tunable magnetism

Benefiting from the atomically thin thickness and uniform surface, controlling magnetism in two-dimensional materials becomes easier than that in bulk materials. Many methods have been adopted to control the magnetism, such as electrostatic doping[5, 6, 28], electric field[4], pressure[29, 30], laser shining[31] and stacking[32]. The tunability of two-dimensional magnetic materials paves ways to new devices for memory.

CrI_3 shows interesting magnetic properties. The intralayer spins show a ferromagnetic coupling and interlayer spins show an antiferromagnetic coupling. In bilayer CrI_3 samples, the ground state at zero magnetic field shows vanishing net magnetization, evidenced by zero Kerr rotation and zero magnetic circular dichroism. By applying electrostatic doping or vertical electric field as shown in Figure 1.7, the balanced state of the two layers was broken and a net magnetization was observed.

The phase transition between antiferromagnetic coupling and ferromagnetic coupling might be used for data storage and computing.

FIGURE 1.7: Electrically tuning magnetism in CrI₃. (a) Applying electric field can tune the interlayer coupling from the antiferromagnetic coupling to ferromagnetic coupling. (b) Electric field controlling of the interlayer coupling of bilayer CrI₃. (c) Electric doping controlling of the interlayer coupling of bilayer CrI₃. Adapted from Reference [4, 5] with permission.

Most two-dimensional ferromagnets suffer from low Curie temperature (T_C) due to large thermal fluctuation. To push the two-dimensional ferromagnets to real applications, room-temperature spontaneous magnetization must be achieved. One method is using ionic gate. The T_C of the pristine bulk Fe₃GeTe₂ is around 202 kelvin. As shown in Figure 1.8, by ionic gating, T_C of a 7-layer flake was increased to room temperature[6], which was even higher than that in the bulk.

Magnetization switching is important in spintronic devices. Spin-up and spin-down

FIGURE 1.8: Gate tuning magnetism in Fe_3GeTe_2 . (a) Magnetic hysteresis loops with $V_g=2.1\text{V}$ at different temperatures. The finite anomalous Hall resistance survives at 310 K. (b) Temperature dependent remanent magnetization at $v_g = 2.1$ V, showing the Curie temperature of 310 K. Adapted from Reference [6] with permission.

are used as information carriers. Electrically switching the spin-up and spin-down state is achieved by spin-transfer torque or spin-orbit torque effects. Magnetization switching ferromagnetism in van der Waals Fe_3GeTe_2 has been demonstrated with spin-orbit layer Pt, Ta and WTe_2 [33, 34]. Benefiting from the atomically flat surface, the magnetization switching is highly efficient.

1.3.3 van der Waals magnetic tunnel junction

Improving the performance of spintronic devices relies on achieving highly efficient spin excitation, spin transport and spin detection. Most spintronic devices are multilayered structures that need to overcome lattice mismatch between layers. The lattice mismatch at the interface not only induces defect, but also limits the device performance. Therefore, lots of efforts have been costed into surface engineering. Van der Waals materials are stacked by van der Waals force and are free from lattice mismatch, which provides a new way to improve the performance of spintronic

devices.

The antiferromagnetic spin ordering between two adjacent CrI_3 layers is a good platform to achieve spin filter effect. As shown in Figure 1.9 a and b, the magnetic tunnel junction built by graphite/ CrI_3 /graphite is demonstrated, which shows a very high tunnel magnetoresistance ratio[35, 36]. The spin-filtering effect in layered CrI_3 , however, is volatile. To achieve nonvolatile data storage, magnetic tunnel junction built by Fe_3GeTe_2 /hBN/ Fe_3GeTe_2 were fabricated as shown in Figure 1.9 c and d[8]. In this structure, the nonvolatile tunnel magnetoresistance ratio was observed when the temperature is below the T_C .

FIGURE 1.9: Magnetic tunneling junction built by two-dimensional magnetic materials. (a) The structure of the graphite/ CrI_3 /graphite device. (b) Tunneling magnetoresistance of the graphite/ CrI_3 /graphite spin valve. (c) Structure of the FGT/hBN/FGT spin valve. (d) Tunneling magnetoresistance of the FGT/hBN/FGT spin valve. Adapted from Reference [7, 8] with permission.

Further improving the performance of two-dimensional van der Waals magnetic

tunnel junctions are needed. One of the challenges is to increase T_C beyond the room temperature. This is crucial for reliable data storage and computing. The second challenge is the high-quality wafer-scale thin film fabrication. The third challenge is to make two-dimensional van der Waals spintronics compatible with traditional complementary metal–oxide–semiconductor technology. Once overcoming these challenges, two-dimensional van der Waals spintronic devices might effectively improve the efficiency of computing and greatly reduce the power cost.

1.3.4 Magnetism with low symmetry

Magnetism in two-dimensional van der Waals materials shows different properties, in which the crystal symmetry plays an important role. Taking bilayer CrI_3 as an example, the broken inversion symmetry due to the antiferromagnetic interlayer coupling leads to giant second harmonic generation[37]. By analysing the polarization resolved angle dependent second harmonic generation, the underlying C_{2h} crystallographic symmetry (monoclinic stacking order) in pristine bilayer CrI_3 was revealed. Another example is the coupled stacking order and interlayer magnetic coupling in bilayer CrBr_3 [32]. These studies pointed out that the magnetism in van der Waals materials is strongly dependent on the crystal symmetry and thus the magnetism in these materials can be manipulated by controlling the staking order in materials.

Raman spectroscopy is an efficient tool to probe the magnetic symmetry and reveal the magnetic phase transition. Xu group used Raman spectroscopy to investigate the impact of the symmetry on magnon physics[9]. As shown in Figure 1.10,

magnon excitation in monolayer CrI_3 was probed by Raman spectroscopy. Cross-polarized Raman spectra at zero magnetic field, -4T and 4T revealed the low-frequency Raman modes of monolayer CrI_3 . The fitted Raman shift at zero magnetic field indicates the magnon energy of the ground state is around 0.3 meV. Optical selection rules of ne-magnon scattering is determined by the three-fold symmetry of the honeycomb lattice of monolayer CrI_3 .

FIGURE 1.10: Magnon excitation in monolayer CrI_3 probed by Raman spectroscopy. (a) Cross-polarized Raman spectra at zero magnetic field, -4T and 4T. (b) Magnetic field dependent Raman shift. The fitted Raman shift at zero magnetic field indicates the magnon energy of the ground state is around 0.3 meV. (c) Optical selection rules of the one-magnon scattering is determined by the three-fold symmetry of the honeycomb lattice of the monolayer CrI_3 . Adapted from Reference [9] with permission.

1.3.5 Detection and manipulation of antiferromagnetism in two-dimensional materials

Antiferromagnetic materials have attracted lots of attentions in the past decade[38]. Owing to the robust magnetic order, intrinsic high antiferromagnetic dynamic frequency and vanishing stray field, antiferromagnetic spintronic devices show potential applications in signal processing, data storage and high-speed computing. In some application areas, antiferromagnetic materials show better performances than that of ferromagnetic materials[39]. However, lack of efficient methods to detect and manipulate the antiferromagnetic order still makes the development of antiferromagnetic spintronics very slow. It turns out that antiferromagnetic two-dimensional van der waals materials shows possibilities to achieve efficient detection and manipulation of the antiferromagnetic order.

Ling group reported the direction of the Néel vector(see Figure 1.11 b) is closely related to the linearly polarized photoluminescence in antiferromagnetic NiPS₃[10]. As shown in Figure 1.11 b, the angle dependent polarized PL shows the two-fold symmetry. The minimum PL intensity corresponds to the Néel vector direction. Applying high magnetic field can align the Néel vector to the same direction as the magnetic field, which is shown in the rotation of the PL pattern. This indicates that PL is an effective probing method to know the Néel vector of the antiferromagnetic NiPS₃. Apart from PL, second harmonic generation (SHG) is another method to probe the Néel vector[11]. As shown in Figure 1.12, the polarization resolved SHG shows the two-fold symmetry, which reveals the two-fold symmetry

FIGURE 1.11: Néel vector direction dependent photoluminescence in antiferromagnetic NiPS₃. (a) Top view of the spin structure of the antiferromagnetic NiPS₃. (b) Applying high in-plane magnetic can align the Néel vector to the direction of the external magnetic field. Adapted from Reference [10] with permission.

of the spin structure of MnPSe₃. By applying the external strain, the polarization resolved SHG pattern changes the direction. This indicates that applying strain is an effective method to tune the Néel vector in MnPSe₃. Meanwhile, SHG in van der Waals MnPSe₃ can be used to image the strain direction of the substrate.

1.3.6 Combined magnetism and topology in two dimensional materials

In topological insulators, the interior is insulating but the surface/edge is conducting. Electrons therefore travel along the surface/edge channels, which is protected

FIGURE 1.12: Imaging and Manipulation of the Néel vector in antiferromagnetic van der Waals MnPSe₃. (a) Spin structure of the antiferromagnetic MnPSe₃. The SHG is excited by the pulsed laser at energy of 1.55 eV. (b) Polarization resolved SHG pattern. (c) Manipulation and imaging the Néel vector. Applying strain can change the direction of the Néel vector. Adapted from Reference [11] with permission.

by time-reversal symmetry. The magnetic order, however, breaks time-reversal symmetry. The combined magnetic order and topology leads to new quantum phenomena, such as quantum anomalous Hall effect.

One way to combine the magnetism and topology is to introduce magnetic order by doping transition metal ions. For example, Xue group reported the quantum anomalous Hall effect in Cr-doped (Bi,Sb)₂Te₃ in 2013[24]. By molecular beam epitaxy (MBE) method, the high quality thin film shows ρ_{xy} of $0.987e^2/h$ and ρ_{xx} of $0.096 e^2/h$ at zero magnetic field and 30 mK. Achieving QAHE is quite challenging in two-dimensional van der Waals materials. In two dimensional material communities, the choice of the topological insulator is very limited. Up to now, only one material, monolayer WTe₂ is confirmed as a topological insulator by experiments. Xu group successfully introduce magnetism in monolayer WTe₂/CrI₃ heterostructure by magnetic proximity effect as shown in Figure 1.13[12]. However,

this is far away from the quantization. In this TI/FM system, the electron flowing in the edge channel shows large nonreciprocal resistance. Apart from introducing

FIGURE 1.13: Nonreciprocal charge transport in $\text{WTe}_2/\text{CrI}_3$ heterostructures. (a) The directional resistance: the resistance at different current shows different values. (b) Non-reciprocal edge transport in the $\text{WTe}_2/\text{CrI}_3$ heterostructure. Adapted from Reference [12] with permission.

magnetic orders by doping and stacking two van der Waals materials, intrinsic magnetic topological insulators then attract many attentions. One is MnBi_2Te_4 family, in which quantum anomalous Hall effect was observed by several groups independently. Another one is the twisted graphene family, where the QAHE was observed at certain filling states.

The layered nature of the van der Waals materials also provides new degree of freedoms, such as the layer degree of freedom, to manipulate physical properties. Van der Waals magnetic topological insulators also show interesting properties beyond QAHE. For example, the intralayer coupling in MnBi_2Te_4 is ferromagnetic, while the interlayer coupling is antiferromagnetic. The magnetic field can therefore

continuously tune the net magnetization of the system. The six-layer MnBi_2Te_4 can be tuned from Chern insulator to Axion insulator by magnetic field[\[19\]](#).

Chapter 2

Ferromagnetism in two-dimensional van der Waals CrBr₃

Atomically thin magnets are the key element to build up spintronics based on two-dimensional materials. The surface nature of two-dimensional ferromagnet opens up opportunities to improve the device performance efficiently. Here, we report the intrinsic ferromagnetism in atomically thin monolayer CrBr₃, directly probed by polarization resolved magneto-photoluminescence. The spontaneous magnetization persists in monolayer CrBr₃ with a Curie temperature of 34 K. The development of magnons by the thermal excitation is in line with the spin-wave theory. We attribute the layer-number dependent hysteresis loops in thick layers to the magnetic domain structures. As a stable monolayer material in air, CrBr₃

provides a convenient platform for fundamental physics and pushes the potential applications of the two-dimensional ferromagnetism.

2.1 Introduction

Ferromagnetism in atomically thin magnet has been studied in a variety of van der Waals materials, including metallic Fe₃GeTe₂[6], semiconducting Cr₂Ge₂Te₆[3] and insulating CrI₃[2]. Even though the long-range magnetic order is highly suppressed by the thermal excitation of magnons in a two-dimensional (2D) magnet at finite temperature, the magnetic anisotropy opens an energy gap in the magnon spectra and therefore, protects the ferromagnetism in two dimensions. The magnon-magnon interaction in such van der Waals ferromagnets also provides a platform to study the fundamental topological spin excitation, for example, Dirac magnon and topological magnon surface state[40]. Moreover, in contrast to the three-dimensional ferromagnet, magnetic 2D materials show tunable magnetic properties due to their surface nature[27]. Particularly the layer-number dependent and gate-tunable magnetism[2, 6], opens a new way to build spintronic devices with high accuracy and efficiency.

Many methods have been adopted to probe the magnetic state of van der Waals magnets, including magneto-optical Kerr effect (MOKE)[2, 3], reflective magnetic circular dichroism (RMCD)[4], X-ray magnetic circular dichroism[41], anomalous Hall effect[6], electron tunnelling[7, 8, 35, 36], magnetic proximity effect[42], scanning tunneling microscope[32], Raman scattering[43] and second harmonic

generation[37]. Apart from them, Xu group reported the helical luminescence in two-dimensional CrI₃, in which the magnetic moment is coupled with the circularly polarized photoluminescence (PL). As shown in Figure 2.1, the PL is excited by a linearly polarized laser at 1.96 eV. The left and right circularly polarized PL was collected separately. After calculating the PL polarization as $\rho = \frac{I_+ - I_-}{I_+ + I_-}$ and plotting the polarization as a function of the magnetic field, the hysteresis loop was observed. This indicated the robust coupling between the spin and the photon, which can be used a convenient method to probe the magnetic moment.

Among various van der Waals ferromagnets, CrBr₃ is an interesting platform to

FIGURE 2.1: Circularly polarized photoluminescence as a function of the external magnetic field. (a) to (d) PL spectra with different magnetic fields. (e) The PL polarization as a function of the magnetic field, which shows the clear hysteresis loop. Adapted from Reference [13] with permission.

study the magnetism in low dimensions and light matter interactions in magnetic materials. The neutron scattering has revealed the Dirac points in bulk CrBr₃,

formed by acoustic and optical spin-wave modes, where both intralayer and interlayer exchange interactions play an important role[40]. On the other hand, optical absorption spectra in CrBr₃ have shown the out-of-plane magnetic field dependence, suggesting potential applications in optoelectronics[44]. However, magnetism in atomically thin CrBr₃, especially in monolayer limit, is still unknown.

In this work, we demonstrate the ferromagnetism in 2D van der Waals CrBr₃. We show the spontaneous magnetization in monolayer CrBr₃, probed by d-d transition induced photoluminescence (PL) with a polarization-resolved optical confocal setup. The magnon excitation is limited at the low temperature region, but shows an exponential development as further increasing the temperature, which is in line with the spin-wave theory. It is worthy to mention that CrBr₃ is much more stable in air as compared to CrI₃ as reported previously, providing a convenient platform for magnetic material applications. Our study also shows the ferromagnetic interlayer coupling and magnetic domain induced hysteresis loops in multilayers, providing an opportunity to use magnetic domains as the information carrier in a van der Waals magnet.

2.2 Methods

2.2.1 Preparation of atomically thin CrBr₃

We fabricated atomically thin CrBr₃ layers by mechanical exfoliation on a quartz substrate in an argon filled glovebox with O₂ and H₂O concentration of less than

1 ppm. Using quartz substrate instead of Si/SiO_2 , can eliminate the effect of PL emission from Si at low temperature. We usually observe the PL emission in the IR range for Si/SiO_2 substrate, which is close to the wavelength of the PL emission of CrBr_3 . We carefully chose the sample with flat surface, so that we can reduce the effect of domain walls pinning on the magnetic properties. The thickness of the sample was firstly estimated by optical contrast and then confirmed by atomic force microscope. The thickness of the monolayer CrBr_3 is around 1 nm and the thickness of the bilayer is around 2 nm as shown in Figure 2.2. For magneto-optical measurements, the sample was transferred into a cryostat equipped with a superconducting magnet. The based temperature is 4 K and the temperature can be controlled by the VTI of the cryostat. The sample is mounted on an attocube positioner. The sample position can be found by a camera.

FIGURE 2.2: AFM images for monolayer and bilayer CrBr_3 . The thickness of the monolayer and bilayer was first examined by the optical contrast and confirmed by AFM. AFM images show the thicknesses of monolayer and bilayer are around 1 and 2 nm, respectively.

2.2.2 Polarization resolved Photoluminescence

To selectively excite and collect the light with a certain polarization, we built up the polarization resolved photoluminescence setup as shown in Figure 2.3. The optical components are: achromatic lenses (AL1-3), polarizers (P1 and P2), half-wave plates (HWP1 and HWP2), quarter-wave plates (QWP1 and QWP2), a short pass filter (SPF), a long pass filter (LPF), and a beam splitter (BS). The sample is placed in a helium bath cryostat with an out-of-plane magnetic field in a Faraday geometry. The excitation laser from the fiber is collimated by AL1. The SPF is to block long-wavelength component in the laser but allow the short-wavelength component. The combination of the P1, HWP1 and QWP1 enables us to manipulate the polarization of the excitation laser with right/left circular polarization or linear polarization. The laser is reflected by a 50:50 BS and is focused on samples via AL3. The PL is also collected by AL3, and then transmitted the BS. The QWP2, HWP2 and P2 are used to select the PL with right/left circular polarization or linear polarization. To block the reflected excitation laser, a SPF is placed before the PL is collected by the fiber via the AL2. The fiber is connected to an avalanche photodiode (APD) or a spectrometer. It's worthy to note that the BS will change the polarization state of the light that passes through it, particularly the reflected light. We calibrate the PL spectroscopy to make sure the light that is reflected by the BS is in the specific state that we need. To calibrate the circularly polarized light, we place a QWP3 and a P3 as shown in Figure 2.4. We set the angle between QWP3 and P3 to be $\pm 45^\circ$. The powermeter is to detect the laser power. When the laser power after P3 is almost zero, we will obtain the circularly polarized light. For linearly

FIGURE 2.3: Optical setup for the polarization-resolved PL spectroscopy.

polarize light with a certain polarization direction, we place a HWP3 in front of the P3. When the laser power after P3 is almost zero, we will obtain the linearly polarized light with a certain polarization direction.

2.2.3 Magneto-optical Kerr effect

Magneto-optical Kerr effect (MOKE) describes when the linearly polarized light is reflected by the material, its polarization vector rotates and becomes elliptical. MOKE arises from the collective effect of the band exchange splitting and spin-orbit interaction, and is widely used in the study of magnetic materials, in particular, imaging the magnetization direction with the μm resolution.

The MOKE is categorized into three types as shown in Figure 2.5. When the

FIGURE 2.4: Calibration for the polarization-resolved PL spectroscopy.

magnetization $\mathbf{M}$ is perpendicular to the sample's surface, it is referred to the polar Kerr effect. When $\mathbf{M}$ is parallel to the surface and in the plane of incidence, it is referred to the longitudinal Kerr effect. When $\mathbf{M}$ is parallel to the surface but perpendicular to the plane of incidence, it is referred to the transverse Kerr effect.

FIGURE 2.5: Polar MOKE, longitudinal MOKE and transverse MOKE

Our MOKE measurement is based on the polar configuration. To increase the resolution, we adopt a lock-in technique. The MOKE setup is shown in Figure 2.6.

The laser is modulated by a photoelastic modulator (PEM) with a base frequency

of 50 kHz, and the reflected light is collected by a photon detector. Both first and second harmonic signals are then analysed by a lock-in amplifier.

FIGURE 2.6: MOKE setup.

2.3 Photoluminescence in CrBr_3

After fabrication, the sample was loaded into a magneto-cryostat (Cryomagnetics close-cycle cryostat) with an out-of-plane magnetic field ranging from -7 T to 7 T. We use a home-made fiber based confocal microscope to perform the polarization resolved PL. Polarizers and waveplates are equipped on the excitation and

collection arms to selectively excite and detect circularly polarized light. The PL spectra are obtained by a spectrometer (Andor Shamrock) with a CCD detector. To measure the hysteresis loops, the PL emission was collected by a single-mode fiber and detected by APD.

FIGURE 2.7: Crystal structure and PL of two-dimensional van der Waals CrBr_3 . a, Top view and side view of the atomic structure of monolayer CrBr_3 . The Cr^{3+} ion was surrounded by six Br^- ions, forming an octahedral environment. The Cr-Br-Cr bond forms an angle of 95.1 degrees. b, PL spectra for CrBr_3 with various thickness. Insert: Optical image of the exfoliated 2D CrBr_3 on a quartz substrate. The scale bar is 15 μm . c, Polarization resolved PL for monolayer CrBr_3 at ± 0.5 T. All PL data were fitted by Gaussian functions.

The atomic structure of monolayer CrBr_3 is shown in Figure 2.7a. Cr^{3+} ions are arranged in a honeycomb lattice, and the Cr-Br-Cr bond forms an angle of 95.1 degrees, suggesting that ferromagnetic superexchange interaction is energetically favorable[45]. To study the magnetism in two dimensions, CrBr_3 flakes were exfoliated on a quartz substrate as shown in the insert of Figure 2.7b. Although in previous studies, reflection and absorption spectra have indicated the presence

of 4T_2 parity forbidden d-d transition, we first experimentally uncovered the d-d transition induced PL at 1.35 eV (Figure 2.7b), excited by a continuous wave (CW) laser at 1.77 eV. All measurements were performed at 2.7 K, unless otherwise specified. We studied the laser power dependent PL under the same polarization configuration (Figure 2.8). The PL intensity scales linearly with the laser power. This linear dependence rules out the possibility that the PL arises from the defect-bond excitons whose PL intensity trends to saturate while increasing the laser power. We further examined the PL spectra for various layer-thicknesses as shown in Figure 2.7b. The PL peak energy almost doesn't change for the thickness ranging from 6 to 73 nm, which suggests a localized transition, in agreement with the d-d transition as an inter-atom transition. According to Laporte rule, d-d transition is parity forbidden. To relax the Laporte rule, symmetry breaking must be introduced, such as spin-orbit coupling, Jahn-Teller distortion and the formation of odd-parity phonons. The broad PL linewidth serves as the evidence for the strong vibronic coupling, resulting in photon sidebands.

The d-d transition in the out-of-plane magnetic field shows circularly selective PL. Figure 2.7 shows the PL in -0.5 T and 0.5 T with $\sigma^+ \sigma^+$ and $\sigma^- \sigma^-$ excitation-collection configurations, where σ^+ (σ^-) represents the left (right) circularly polarized light. The PL at ± 0.5 T shows opposite helicity, indicating that the spin of electrons in CrBr₃ is coupled to the circularly polarized light.

FIGURE 2.8: PL intensity as a function of the excitation laser power with a linear fitting. The PL intensity as a function of the laser power for monolayer is used to rule out the effect of defect on PL. The PL emission was collected by a single-mode fibre and detected by the APD. The linear dependence indicates that the PL doesn't arise from the defect-bound excitons, whose PL intensity trends to saturate at a high excitation power.

2.4 Ferromagnetism in monolayer CrBr₃

The thickness of monolayer CrBr₃ is around 1 nm, determined by AFM (Figure 2.2). To precisely detect the magneto-PL in a single magnetic domain, the PL emission was collected by a single-mode optical fiber and detected by an APD. The polarization of the PL is calculated by $\rho = \frac{I_{\uparrow} - I_{\downarrow}}{I_{\uparrow} + I_{\downarrow}}$, which is proportional to the magnetic moments, where I is the PL intensity recorded by APD while sweeping the magnetic field, and $I_{\uparrow}(I_{\downarrow})$ is the PL intensity for fully spin up (down) states. Here, we show how we calculated the polarization through the PL intensity in Figure 2.9. Figure 2.10 shows the polarization as a function of the magnetic field under $\sigma^+ \sigma^+$, $\sigma^- \sigma^-$, $\sigma^+ \sigma^-$, and $\sigma^- \sigma^+$ configurations. The green symbols show the evolution of the PL intensity with the magnetic field sweeping from 0.1 to -0.1 T, and the orange symbols show the time reversal process.

We first discuss the polarization resolved PL as a function of the magnetic field.

FIGURE 2.9: (a) PL intensity as a function of the magnetic field. The PL intensity was recorded by an APD. (b) Polarization as a function of the magnetic field. To quantitatively represent the magnetization, we define the polarization as $\rho = \frac{I - (I_{\uparrow} + I_{\downarrow})/2}{(I_{\uparrow} + I_{\downarrow})/2}$ is the PL intensity where the spin is fully polarized up (down).

There are three features in the Figure 2.10a: (i) The polarization abruptly increases or decreases within a narrow field range; (ii) Except the points near the transition field, the polarization is almost independent to the magnetic field; (iii) The hysteresis loops have the same shape with the same excitation polarization, and it is independent to the polarization of the collection. We attribute these observations to the circularly selective absorption as shown in Figure 2.10b. Taking $\sigma^+ \sigma^+$ configuration as an example, at 0.1 T the electrons with up-spin selectively absorb the σ^+ light and are excited to the upper states. As the magnetic field is swept to a negatively large point, thereby flipping the spin, less electrons can be excited by the σ^+ light. Therefore, the polarization suddenly drops. And in the time reversal process, the polarization shows a rapid increase at a certain field. The collection-polarization independent hysteresis loop is assigned to the depolarization

FIGURE 2.10: Ferromagnetism in monolayer CrBr₃. a, Polarization as a function of the magnetic field. The orange symbols show the polarization as the magnetic field is swept from -0.1 T to 0.1 T and the green symbols show the polarization as the magnetic field is swept from 0.1 T to -0.1 T. The non-zero polarization at zero magnetic field indicates the spontaneous magnetization. σ^+ σ^- is the left (right) circularly polarized light. b, Origin of the magnetic field dependent PL. The helicity of the absorption ties to the spin of the electrons at the ground states. The unbalance of the spin-up and spin-down states makes a higher σ^+ / σ^- absorption and eventually leads to the high/low PL emission. Due to the phonon scattering at the excited state, the output light is depolarized (ϕ). c, Hysteresis loops at various temperature. The hysteresis loop disappears as the temperature was increased above the Curie temperature TC at 34 K, slight lower than that of the bulk crystal.

of electrons at the excited state due to the electron-phonon scattering. This is in consistence with the strong vibronic coupling in the d-d transition. This electric dipole transition provides a way to optically probe the magnetic state of the 2D CrBr₃.

The non-zero polarization at zero magnetic field (0 T) indicates the presence of spontaneous magnetization in monolayer CrBr₃. To further confirm the intrinsic ferromagnetism, we measured the hysteresis loops with various laser powers ranging from 10 to 100 μ W (Figure 2.9). While shining high-power laser, the sample temperature might change and influence the magnetic state. Figure 2.9 shows the laser power independent hysteresis loops, which indicates the heating effect is very

FIGURE 2.11: Hysteresis loops at various excitation laser powers. The left column shows the APD count as a function of the magnetic field under σ^+ configuration, and the left column shows the calculated polarization as a function of the magnetic field. By studying the laser power dependent hysteresis loops, we rule out the effect of thermal excitation on magnetism. Furthermore, the polarization is almost independent to the laser power, indicating that the defined polarization is proportional to the magnetization.

weak in our measurement. Even though the APD count increases with the excitation power, the polarization as a function of the magnetic field doesn't change much. The laser power independent hysteresis loops rule out the effect of thermal excitation on the magnetization. We also studied the magneto-optical Kerr effect (MOKE) in the monolayer CrBr₃ on the Si/SiO₂ substrate as shown in Figure 2.12, which agrees with magnetic hysteresis loops probed by PL.

The ferromagnetism in monolayer results from the Cr-Br-Cr superexchange in-

FIGURE 2.12: MOKE for two-dimensional CrBr₃. To further confirm the ferromagnetism in two-dimensional CrBr₃, we also performed MOKE measurements. (a), (b) and (c) show MOKE for CrBr₃ with various thickness. CrBr₃ flakes were exfoliated on Si/SiO₂ substrates and then loaded into a magneto-cryostat (Cryomagnetics close-cycle cryostat). The magnetic field was applied in the out-of-plane direction. The incident laser with the wavelength of 405 nm was adopted to perform the MOKE measurement and the laser power was 12 μ W. The MOKE results agree well with the magnetic hysteresis loops probed by PL, indicating that the direct PL probing ferromagnetism is reliable.

teraction. In monolayer CrBr₃, six Cr³⁺ ions form a honeycomb structure and each Cr³⁺ ion is surrounded by six Br⁻, forming an octahedral environment (Figure 2.7). In this crystal field, the degeneracy of d orbit of Cr atom is lifted and the d level splits into t_{2g} and e_g bands. Three spin polarized electrons occupy the t_{2g} band according to Hund's first rule. Therefore, the magnetic moment each Cr³⁺ ion yields is $\sim 3\mu_B$, corresponding to the polarization of 0.175 in monolayer case. The magnetic moments of monolayer CrBr₃ align in the out-of-plane

direction. The XXZ spin Hamiltonian [46] is adopted to describe the 2D ferromagnet: $H_{spin} = -A \sum_i (S_i^Z)^2 - J \sum_{i,j} S_i S_j - \lambda \sum_{i,j} S_i^Z S_j^Z$ where A is the single-ion anisotropy term, J is the Heisenberg exchange term and λ is the anisotropic exchange term. The quenched d-orbit results in a negligible single-ion anisotropy term and thereby A is almost zero. The angle of the Cr-Br-Cr bond is around 90 degrees, which favors a ferromagnetic intralayer coupling and $J > 0$. The out-of-plane magnetic anisotropy corresponds to $\lambda > 0$.

FIGURE 2.13: The polarization as a function of temperature for monolayer CrBr₃. The data is fitted by $\rho(T) \sim S - \frac{k_B T}{2\pi JS} e^{-\Delta_0/k_B T}$. Inset: Spin wave excited by the thermal fluctuation, which accounts for the decay of the polarization as increasing the temperature.

The Curie temperature was experimentally determined by measuring the hysteresis loops at various temperatures (Figure 2.13). When the temperature was increased above the Curie temperature at 34 K, a ferromagnetism-to-paramagnetism phase transition occurred. The T_C of 34 K is only slightly lower than that of the bulk (i.e. 37 K). Figure 2.13 shows the polarization as a function of the temperature. The excitation of magnon by thermal fluctuation degrades the long-range magnetic order. We describe the reduced polarization as increasing the temperature within a spin-wave theory. In an isotropic 2D spin system, the gapless magnon spectra leads

to the absence of the spontaneous magnetization at finite temperature. Nevertheless, Δ_0 , the spin wave gap opens by the anisotropic energy, protects the long-range magnetic order, which plays an essential role in the 2D ferromagnet. The magnetization in units of $\hbar$ per Cr atom as a function of the temperature is described as: $M(T) \sim S - \frac{k_B T}{2\pi JS} e^{-\Delta_0/k_B T}$, where $S = 3/2$, and k_B is Boltzmann constant. The polarization ρ is proportional to the M : $\rho(T) \sim S - \frac{k_B T}{2\pi JS} e^{-\Delta_0/k_B T}$. The solid line in Figure 2.13 shows the fitting results with this model, in line with our experimental data. In the low temperature region ($< 15\text{K}$), the polarization weakly depends on the temperature. Further increasing the temperature leads to an exponential development of magnons and the polarization rapidly decreases until vanishing at the T_C .

2.5 Ferromagnetic interlayer coupling and layer dependent magnetism in multilayer CrBr₃

Next, we study the layer-layer interaction in 2D van der Waals CrBr₃. The interlayer coupling is revealed by a bilayer CrBr₃ with the thickness of about 2 nm, determined by AFM (Figure 2.2). Distinct from bilayer CrI₃, whose interlayer coupling at the ground states was antiferromagnetic, bilayer CrBr₃ preserves ferromagnetism as shown in Figure 2.14(a), suggesting a ferromagnetic interlayer coupling. Note that the transition field for bilayer CrBr₃ from fully spin up states to fully spin down states, is almost one order smaller than that for bilayer CrI₃. This is in line with the different anisotropic energies of these two ferromagnetic

insulators.

FIGURE 2.14: Layer dependent magnetism in CrBr₃. a. The hysteresis loop for bilayer CrBr₃. A non-zero polarization at zero magnetic field indicates a ferromagnetic interlayer coupling. b. The polarization as a function of the magnetic field for 8 nm, 54 nm and 73 nm CrBr₃. The formation of the strip- or honeycomb-like magnetic domains may account for the layer dependent magnetism in CrBr₃.

Finally, we discuss the magnetism in multilayer CrBr₃. Figure 2.14b shows the polarization as a function of the magnetic field for 8, 54 and 73 nm samples. Different from the thin sample, whose rectangular hysteresis loops indicate single-domain and fully out-of-plane anisotropic magnetic ordering, the polarization of

thicker CrBr₃ samples vanishes at 0 T. As the magnetic field was increased, the polarization became saturated after reaching a transition field, being similar to that of previously reported multilayer Fe₃GeTe₂ and Co/Pt thin films[25, 47]. We attribute this magnetic behavior to the formation of strip- and honeycomb-like magnetic domain structures as reported in [47], which is beyond the resolution of the PL setup. The spot size of our excitation laser is about 1 μm , and thereby the polarization is contributed by several domains. As a result, the polarization at 0 T vanishes and shows a gradual evolution as increasing the magnetic field, and abruptly saturates at a certain magnetic field. The possible reason for forming this kind of domains might be the low out-of-plane anisotropic energy in thick CrBr₃. Even in a very low temperature (2.5K), the ratio of out-of-plane anisotropy to the exchange interaction is strongly dependent on the dimension. The enhanced out-of-plane anisotropy in thin layers might result from a reduced screening effect. Even though we could expect a higher T_C with a larger out-of-plane anisotropy, the competition of the increased thermal fluctuation in thin layers eventually makes the T_C slightly lower than that of bulk. The temperature dependent hysteresis loops of bilayer CrBr₃ and 73-nm CrBr₃ is shown in Figure 2.15.

2.6 Conclusion

To conclude, we demonstrate ferromagnetism in atomically thin CrBr₃ through polarization resolved magneto-PL. In monolayer CrBr₃, a rectangular hysteresis loop shows the spontaneous magnetization persists despite the thermal fluctuation.

FIGURE 2.15: Temperature dependent hysteresis loops for bilayer and 73 nm CrBr₃. The Curie temperatures of the bilayer and 73 nm CrBr₃ were determined by increasing the temperature until the hysteresis loops disappeared. The TC for bilayer is around 35 K. The TC for 73 nm sample is around 37 K, the same as bulk CrBr₃ as reported previously.

The polarization vanishes at 34 K due to the excitation of magnons. We also reveal the ferromagnetic interlayer coupling in a bilayer. Finally, the hysteresis loops of thick layers are assigned to the formation of strip- and honeycomb- like magnetic domains, whose magnetization is strongly dependent on the layer number of CrBr₃. Our study uncovers the magnetism in 2D CrBr₃ and might pave a way for novel opto-electronic and spintronic devices.

Chapter 3

Magnetic proximity effect in graphene/CrBr₃ van der Waals heterostructures

2D van der Waals heterostructures serve as a promising platform to exploit various physical phenomena in a diverse range of novel spintronic device applications[27, 48]. Efficient spin injection is the prerequisite for these devices. The recent discovery of magnetic 2D materials leads to the possibility of fully 2D van der Waals spintronics devices by implementing spin injection through the magnetic proximity effect (MPE). Here, the investigation of MPE in 2D graphene/CrBr₃ van der Waals heterostructures is reported, which is probed by the Zeeman spin Hall effect through non-local measurements. Quantitative estimation of the Zeeman splitting

field demonstrates a significant MPE field even in a low magnetic field. Furthermore, the observed anomalous longitudinal resistance changes at the Dirac point $R_{XX,D}$ with increasing magnetic field near $\nu = 0$ may be attributed to the MPE-induced new ground state phases. This MPE revealed in the graphene/CrBr₃ van der Waals heterostructures therefore provides a solid physics basis and key functionality for next-generation 2D spin logic and memory devices.

3.1 Introduction

The exploration of the spin degree of freedom holds promise for next-generation memory and logic devices[27, 48]. These devices use spins to carry information instead of charges and therefore can lead to low-power, high-speed operations. Graphene provides an interesting platform for spintronics with the unique advantages of a long spin lifetime and long spin transport distance[49]. For spintronic devices, spin initialization is a prerequisite. There are three main methods for spin injection in graphene. First, conducting ferromagnetic electrodes directly on graphene can lead to efficient spin injection. However, it suffers from the drawback of naturally short-circuiting the graphene layer and restricting the design of spin switches. Second, magnetic dopants can be introduced into graphene. It can lead to the degradation of its unique property of high carrier mobility. Therefore, a lot of efforts have been devoted to the third method, that is, the introduction of magnetism in graphene with the proximity effect in the interface of magnetic insulators and graphene. Pioneer works have been demonstrated with 3D bulk

magnetic insulators like yttrium iron garnet (YIG), europium (II) sulfide, and bismuth ferrite[14, 50]. As shown in Figure 3.1, the anomalous Hall effect observed in graphene/YIG indicates the strong magnetic proximity effect.

FIGURE 3.1: Magnetic proximity effect in graphene/YIG heterostructures. (a) shows the device structure of the graphene/YIG heterostructure. (b) shows the anomalous Hall effect in graphene induced by the MPE. Adapted from Reference [14] with permission.

Due to the short-range nature of the magnetic exchange coupling, a fully 2D van der Waals heterostructures is desired for downsizing the device and introducing magnetic proximity effect (MPE) at the same time. The recent profound discoveries of 2D ferromagnets bring the possibility of 2D ferromagnetic van der Waals heterostructures, it is urgent and essential to comprehensively investigate the magnetic coupling between graphene and 2D ferromagnetic materials for developing 2D spintronic devices. Not just the evidence of the existence of MPE in 2D ferromagnetic van der Waals heterostructures, here, we report the direct observation of MPE in graphene/CrBr₃ van der Waals heterostructures by probing Zeeman spin Hall effect (ZSHE) through non-local transport measurements. A further quantitative estimation of Zeeman splitting field demonstrates a significant magnetic proximity exchange field even in a low magnetic field. Furthermore, we observe

anomalous longitudinal resistance changes at the Dirac point $R_{XX,D}$ with increasing external magnetic field near $\nu = 0$. This may attribute to the MPE induced ground state phases transformation of graphene from the ferromagnetic state at the lower magnetic field and a canted antiferromagnetic state at a higher field in quantum Hall regime.

3.2 Method

A typical graphene/CrBr₃ van der Waals heterostructure with Hall bar structure for electrical transport measurement is fabricated as shown in Figure 3.2a. In order to reach the best performance and a substantial MPE in graphene/CrBr₃ heterostructures, we optimize the fabrication process and conditions to achieve the desired heterostructures. The sample in the final stage is encapsulated and protected by poly(methyl methacrylate) (PMMA), which keeps the device surface away from the moisture and air for cryotemperature tests. The atomic structure of layered CrBr₃ is shown in Figure 3.2b. The Cr³⁺ ions are configured in a honeycomb network, and the green arrows represent the spin direction of Cr atoms, which are found to exhibit a strong ferromagnetic coupling. The Raman spectra of Figure 3.2c indicates that the monolayer graphene still preserves a high crystal quality when heterostructured with CrBr₃ layer. The optical image in Figure 3.2d displays the asfabricated graphene/CrBr₃ heterostructures, along with the H-shape Hall bar structure for conducting non-local measurements.

The natural graphite and CrBr₃ crystals were purchased from HQ graphene. First,

FIGURE 3.2: Fabrication and characterization of graphene/CrBr₃ van der Waals heterostructures. a) Scheme of graphene/CrBr₃ heterostructures configuration. b) Atomic structure of very thin CrBr₃ layers. Purple atoms: chromium; brown atoms: bromide. The green arrow shows the spin direction of Cr³⁺ atoms. c) Raman spectrum of as-fabricated graphene/CrBr₃ van der Waals heterostructures without top protective cover (the black dashed area is graphene; green dashed area is CrBr₃). d) Optical image of the as-prepared graphene/CrBr₃ heterostructures. The scale bar is 5 μm.

a monolayer graphene sheet was exfoliated and transferred onto a 285 nm SiO₂/Si substrate by using conventional scotch tape mechanical exfoliation method, the thickness of monolayer graphene was identified by its optical contrast on SiO₂/Si substrate with an optical microscope and then confirmed by Raman spectroscopy. For electrical transport measurement of graphene/CrBr₃ van der Waals heterostructures, subsequently, electron-beam lithography, metal deposition, and lift-off process were used to deposit Cr/Au electrodes (10 nm/20 nm) on the graphene layer, followed by using electron-beam lithography again and oxygen plasma etching to form Hall bar structure of graphene. Both acetone and isopropanol washing followed by a vacuum annealing were adopted to remove the PMMA residues from graphene after contact formation and Hall bar patterning, this step is important

because any residue on the graphene surface will not allow a good interface between CrBr₃ and graphene. Note that during the heterostructures assembly and contact processing, CrBr₃ is not initially stacked on graphene layer because the electrodes fabricating process (especially the electron-beam exposure, plasma etching, and subsequent lift-off process) would seriously damage the CrBr₃. As to obtain a few CrBr₃ layers, the CrBr₃ crystal was first exfoliated onto a poly(dimethylsiloxane) (PDMS) stamp in an inert atmosphere glove box with less than 0.1 ppm water and oxygen. Similarly, very thin CrBr₃ layers of different thicknesses were identified by using the optical contrast under different color filters and dark-field imaging. After that, a 10 nm thick CrBr₃ layer was picked up by a PDMS stamp in the glove box and transferred into the graphene Hall bar channel. Since only the clean side of CrBr₃ layer contacted with graphene, there was no PDMS residual issue in the heterostructures, which could be a problem of realizing magnetic proximity. Finally, the protective and insulated thin PMMA membrane was coated onto the CrBr₃/graphene/substrate to achieve the desired graphene/CrBr₃ van der Waals heterostructures. Here it is important to choose a CrBr₃ layer which fits the whole Hall bar channel to guarantee it also has good contact with graphene near the contact edges.

Transport and magnetotransport measurements were performed in a Physical Property Measurement System (Model 6000) with temperature down to 2 K and magnetic field up to 9 T. The nonlocal and four-terminal longitudinal electrical resistances were acquired using a Keithley 2182A nanovoltmeter and a Keithley 2636B

source meter with excitation current of 0.5 μA for high accurate electrical measurements. Multiple devices were prepared and measured.

3.3 Magnetic proximity effect in graphene/CrBr₃ heterostructure

As shown in Figure 3.3a, with the Zeeman effect, the splitting of the Dirac cone in graphene generates electron and hole-like carriers with opposite spins near the Dirac point. This property can induce ZSHE, with the working principle shown in Figure 3.3b. First, a source-drain current I is applied in the presence of an external perpendicular magnetic field, because the Lorentz force has opposite signs for electrons and holes, the net charge current is zero and hence no net transverse charge current is produced in the sample. However, the net spin current is nonzero (Figure 3.3b). With this configuration, a non-local voltage V_{nl} can be measured in the remote regions. With a larger magnetic field, we expect to observe a larger V_{nl} . Therefore, we could probe the MPE in graphene/CrBr₃ heterostructures via the V_{nl} induced by ZSHE in graphene layer.

The observation of MPE in graphene/CrBr₃ heterostructures through ZSHE is shown in Figure 3.3c and d. The acquired non-local resistances $R_{nl} = V_{nl}/I$ as a function of the back-gate bias V_g under a series of external fields at temperature of 2 K are plotted in Figure 3.3. The R_{nl} peak at the Dirac point is written as $R_{nl,D}$. Along with the external magnetic field increasing, the non-local resistance $R_{nl,D}$

FIGURE 3.3: Zeeman spin Hall effect and non-local measurements in graphene/CrBr₃ heterostructures. (a) Schematic diagram of Zeeman splitting of the Dirac cone in monolayer graphene (arrow represents the carrier spin direction). (b) Working principle of typical non-local measurements for probing Zeeman spin Hall effect. The driven current produces transverse spin up (red) and spin down (blue) currents under an external perpendicular magnetic field, the resulting imbalance of net spin current can reach remote regions and generate a voltage drop V_{nl} . (c) The non-local resistance R_{nl} as a function of the back gate V_g acquired under different external field for the graphene/CrBr₃ heterostructures. The sharp increase of $R_{nl,D}$ (R_{nl} at Dirac point) with magnetic field suggests a strong Zeeman splitting energy enhancement. (d) Temperature dependence of $R_{nl,D}$ in graphene/CrBr₃ heterostructures shows an abrupt slowdown as the temperature exceeds the transition temperature T_C (≈ 37 K) of CrBr₃, which attributes to the CrBr₃'s phase change from ferromagnetic to paramagnetic state, while the $R_{nl,D}$ of pure graphene showing a very small and monotonic decrease without such perceptible onset feature. All $R_{nl,D}$ data set is taken at $\mu_0 H = 4$ T

rises sharply, suggesting a distinct Zeeman splitting energy enhancement. Moreover, other possible source of producing non-local signal like ohmic contribution were analyzed and excluded. As to the finite V_{nl} at 0 T, it may be due to the spin Hall effect caused by spin polarization which is induced by the exchange field under 0 T since the magnetic hysteresis of 2D CrBr₃ and EuS is different, CrBr₃ has a non-zero remanence but EuS is zero at zero applied field. Therefore, this

feature enables the prospect of utilizing novel devices without external magnetic field which cannot be generated on nano spatial scales. In order to confirm the origin of this Zeeman splitting energy enhancement resulting from the MPE, we further measured the temperature dependence of $R_{nl,D}$. Figure 3.3d indicates that $R_{nl,D}$ in graphene/CrBr₃ heterostructures experiences an abrupt slowdown as the temperature exceeds at about 37 K, corresponding to the transition temperature T_C of CrBr₃ which has a phase change from ferromagnetic to paramagnetic state. In contrast, pure graphene shows a very weak temperature dependence without distinguishable onset feature like graphene/CrBr₃ heterostructures. Undoubtedly, we can therefore conclude that the MPE is the dominating contribution to induce $R_{nl,D}$ in graphene/CrBr₃ heterostructures when the temperature is lower than the T_C of CrBr₃.

FIGURE 3.4: Magnetic field dependence measurement and the theoretical calculation of the MPE induced Zeeman splitting energy in graphene/CrBr₃ van der Waals heterostructures. (a) The plot of $R_{nl,D}$ changes (using $R_{nl,D}(0\text{ T})$ as reference for comparison) with external magnetic field sweep measured at 2 K. It can be seen that $R_{nl,D}$ of graphene/CrBr₃ heterostructures rises sharply with external magnetic field increasing, reaches up to orders-of-magnitude enhancement as against pristine graphene. Inset curve is R_{nl} of graphene/CrBr₃ heterostructures as a function of V_g under 4 T. (b) Calculated Zeeman splitting energy E_Z and corresponding Zeeman field B_Z is plotted against the external magnetic field, respectively. The inset shows field-effect mobility μ as a function of carrier density of graphene/CrBr₃ heterostructures.

Using as described Zeeman spin Hall probing, magnetic field dependence measurement and related theoretical calculation of the magnetic field induced Zeeman splitting energy in graphene/CrBr₃ could provide quantitative information on MPE in the 2D van der Waals heterostructures. Figure 3.4a is the plot of $R_{nl,D}$ changes (data were divided by $R_{nl,D}(0 \text{ T})$ for comparison purpose) with external magnetic field sweep measured at 2 K. It can be observed that $R_{nl,D}$ of graphene/CrBr₃ heterostructures reaches orders-of-magnitude increase with respect to the magnetic field from 0 to 4 T comparing with pristine graphene. Inset curve is the measured R_{nl} of heterostructures as a function of V_g under 4 T. The quantitative description of MPE in graphene/CrBr₃ heterostructures can be estimated by calculating its Zeeman splitting energy E_Z and the total Zeeman field B_Z . We first adopt the definition of R_{nl} as follows, according to:

$$R_{nl} = \frac{dV_{nl}}{dI} \propto \frac{1}{\rho_{xx}} \left(\frac{\partial \rho_{xy}}{\partial \mu} E_Z \right)^2 \quad (3.1)$$

where ρ_{xx} and ρ_{xy} is the longitudinal and Hall resistivity, respectively. Both are strongly depending on the external out of plane magnetic field ($B_{\perp}$); μ is the chemical potential, E_Z is the Zeeman splitting energy which is proportional to the total external field (B). Therefore, we have $R_{nl} = \beta(B_{\perp} B^2)$, β represents the ρ_{xx} and ρ_{xy} manifested parameters. The R_{nl} peak at the Dirac point $R_{nl,D}$ could be further written as $R_{nl} = R_0 + \beta(B_{\perp}) E_Z^2$, R_0 stands for the non-local resistance of non ZSHE signal at zero field. Moreover, the $E_Z = g\mu_B B_Z = g\mu_B (B_{MPE} + B(\mu_0 H))$

can be further written as

$$E_Z = E_{Z0} \cdot \frac{\sqrt{(1 + \mu_*^2 B^2) B_0^2}}{\sqrt{(1 + \mu_*^2 B_0^2) B^2}} \times \frac{\sqrt{(R_{nl,D} B - R_0)}}{\sqrt{(R_{nl,D} (B_0 - R_0))}} \quad (3.2)$$

where μ_* is the carrier mobility, B_0 is the zero magnetic field, B_{MPE} represents the field induced by MPE in graphene/CrBr₃ heterostructures.

The calculation of the effective Zeeman energy following [51] can be written as:

Theoretically, the non-local resistance predicted for the ZSHE is:

$$R_{nl} \propto \frac{1}{\rho_{xx}} \left(\frac{\partial \rho_{xy}}{\partial \mu} E_Z \right)^2, \quad (3.3)$$

where R_{nl} is defined as the non-local resistance, μ is the chemical potential, ρ_{xx} and ρ_{xy} is the longitudinal and Hall resistivity, respectively; E_Z is the Zeeman splitting energy. While the non-local resistance at Dirac point R_{nl} can be further written as

$$R_{nl,D} = R_0 + \beta(B_0) E_Z^2, \quad (3.4)$$

where R_0 stands for the non-local resistance at zero-field, β represents the ρ_{xx} and ρ_{xy} manifested parameters. To directly derive the expression between E_Z and $R_{nl,D}$ at the different external magnetic field, we introduce the parameter α , which is determined by

$$\alpha(B) = \sqrt{\frac{\beta(B)}{\beta(0)}} = \frac{E_{Z0}}{E_Z} \sqrt{\frac{R_{nl,D}(B) - R_0}{R_{nl,D}(B_0) - R_0}}. \quad (3.5)$$

For evaluating E_Z conveniently, we similarly choose a proper magnetic field B_0 as a reference to calculate E_Z . While β has the following form based on the given formulas above

$$\beta = \frac{\omega}{2l_s} e^{-\frac{1}{l_s}} \frac{1}{\rho_{xx,D}} \left(\frac{\partial \rho_{xy}}{\partial \mu} \right)^2 \Big|_{\mu=\mu_D} \quad (3.6)$$

where ρ_{xx} and ρ_{xy} are dependent on magnetic field, other parameters are not. By considering the behavior at charge neutral point, ρ_{xx} is a sum of the Drude-Lorentz resistivity and the electron-hole drag contribution, and thus $\rho_{xx,D}$ is estimated as

$$\rho_{xx,D} = \frac{m_T}{2n_T e^2 \tau} (1 + \tau^2 \Omega^2) \quad (3.7)$$

$$n_T = \frac{\pi}{12} \frac{K_B^2 T^2}{\hbar^2 v_0^2} \quad (3.8)$$

where $m_T \propto 3.29 K_B T / v_0^2$, n_T is the density of thermally activated electrons (holes) at the charge neutral point, τ is the scattering time, and Ω is the cyclotron frequency, v_0 is Fermi velocity. Finally, the parameter α can be written as:

$$\alpha(B) = \frac{\sqrt{(1 + \mu_*^2 B_0^2) B^2}}{\sqrt{(1 + \mu_*^2 B^2) B_0^2}}. \quad (3.9)$$

The the E_Z can be written as:

$$E_Z = E_{Z0} \cdot \frac{\sqrt{(1 + \mu_*^2 B^2) B_0^2}}{\sqrt{(1 + \mu_*^2 B_0^2) B^2}} \times \frac{\sqrt{(R_{nl,D} B - R_0)}}{\sqrt{(R_{nl,D} (B_0 - R_0))}} \quad (3.10)$$

For the convenience of calculating E_Z , we have an approximation of $E_{Z0} \approx g\mu_B B_0$ by neglecting the MPE field contribution and using $B_0 = 0.1T$ as reference magnetic field to estimate the lower-bound of E_Z . The calculated Zeeman splitting energy E_Z and its corresponding Zeeman field B_Z are plotted against the external magnetic field in Figure 3.4, respectively. The inset provides field effect mobility μ_* versus carrier density of graphene/CrBr₃ heterostructures. High carrier mobility ensures the excellent device performance of 2D magnetic coupling and further observation of pronounced quantum oscillations. Figure 3.4b shows a clear evidence of the substantial magnetic exchange field by presenting two little different slopes of line segments as well as the magnetic field increasing. Since the magnetic exchange field is nearly irrelevant to the external field $B_\perp$, when the applied field is low and less than about 1 T, the line slope is a bit steeper than the one with field larger than 1 T, which demonstrates that magnetic exchange field is the dominating contribution to the nonlocal resistance at low field. Giving $\mu_0 H = 4$ T, the estimated B_Z is approximately twice of the applied field, which seems weaker than other reported 2D or graphene/ferromagnetic material systems like WSe₂/EuS, graphene/EuS, and graphene/BiFeO₃, but this result is reasonable, because 2D CrBr₃ has a smaller interlayer exchange coupling energy $J = 1.56$ meV, and its magnetic moment per Cr ion is $3.25 \mu_B$, comparing with EuS which has an exchange coupling energy $J \approx 1.56$ meV, and the magnetic moment per Eu ion is $7.9 \mu_B$. As shown in Figure 3.5, four-probe longitudinal resistivity measurement further reveals the MPE effect in the quantum Hall regime of graphene/CrBr₃ heterostructures, which not only lifts the ground state degeneracy of graphene but also

FIGURE 3.5: MPE effect in the quantum Hall regime of graphene/CrBr₃ heterostructures. (a) Color map showing the longitudinal resistance R_{XX} as a function of the gate bias V_g and the applied magnetic field $\mu_0 H$, which is measured at 2 K. (b) Extracted longitudinal resistance under external field from 2 to 9 T from (a). For clarity of labelling the Landau level filling factors, resistance curves are vertically shifted and are proportional to the applied magnetic field. (c) Longitudinal resistance R_{XX} measured at 9 T shows pronounced quantum oscillations. ν is directly derived from the longitudinal resistance versus gate bias curve at each local R_{XX} minimum, and all ν are labelled in light gray. The inset figure shows V_g is linear to each ν . (d) The theoretical predictions (dashed lines) by using the capacitance model and experimental results (solid scatters with error bar) of gate bias with magnetic field at $\nu = \pm 2$. (e) The close-up of each local R_{XX} maxima and R_{XY} minima of resistance curves taken at 2, 3, and 4 T, revealing an anomalous resistance dip and peak-splitting features at $\nu = 0$ that develop with the increasing magnetic field, which suggests the lifting of Landau level degeneracy under large B_Z .

indicates the ground state phase transformation near $\nu = 0$ in the quantum Hall regime. Color map of Figure 3.5a shows a typical Landau fan of the longitudinal resistance R_{XX} as a function of the gate bias V_g and the applied magnetic field $B(\mu_0 H)$. Similar to the quantum mobility measurement of graphene in previous report, the central bright region near the Dirac point suggests that a gap is opened when the magnetic field is larger than 5 T. We further extract longitudinal resistance measured under external field from 2 to 9 T as shown in Figure 3.5b. For clarity of labelling the Landau level filling factors, resistance curves are vertically shifted and are proportional to the applied magnetic field. The filling factor ν of the Landau level can be obtained by using $\nu = \pm 4(|n| + \frac{1}{2})$ where $n = 0, 1, 2, \dots$ is the Landau level index. As shown in Figure 3.5c, ν can be directly derived from the longitudinal resistivity versus gate bias curve at each local R_{XX} minimum, which shows pronounced quantum oscillations. Inset figure manifests that V_g is linearly proportional to each ν value, as expected. Since the injected carriers by gate voltage into graphene could be expressed with $\frac{e^2 B}{h}$, we could therefore use capacitance model to calculate the gate voltage ($V_g - V_D$) or the corresponding electron density with magnetic field at $\nu = \pm 2$ as the result shown in Figure 3.5 (gray dashed lines). However, the obtained predication only considers the applied field $B(\mu_0 H)$ contribution, which is not consistent with the experimental data (blue and red symbols) within the error bar, proving that the contribution from induced exchange field by CrBr₃ is remarkable. Most importantly, the close-up of each local R_{XX} maxima and R_{XX} minima of resistance curves taken at 2, 3, and 4 T in Figure 3.5e reveal an anomalous resistance dip and peak-splitting features at

$\nu = 0$ that develop with the increasing magnetic field, suggesting the lifting of Landau level degeneracy under large B_Z with the contribution from MPE between CrBr₃ and graphene. Furthermore, we observed the anomalous longitudinal resistance at the Dirac point $R_{XX,D}$ with increasing magnetic field, which results from the MPE induced B_Z in graphene/CrBr₃ heterostructures, and attributes to the ground state phases of graphene transition from a ferromagnetic state to a canted antiferromagnetic state near $\nu = 2$.

In addition, the origin of MPE at the interface of graphene/CrBr₃ van der Waals heterostructures can be explained by a recent first-principle calculated model on the MPE in 2D graphene/CrBr₃ heterostructure. MPE which is strongly dependent on the orbital hybridization at the interface, arises from the spin dependent interlayer coupling and results in the overall spin polarization to 63.6% in the heterostructure system by calculating its electronic structure of the graphene/CrBr₃ heterolayer, and a further perpendicular gating electric field can tune the miniband spin splitting. The theoretical predications agree with the observation of a large non-zero spin Hall effect signal at zero field in this work due to spin polarization in graphene/CrBr₃ heterostructure. Furthermore, by extracting exchange coupling fields from Hanle spin precession measurements calculation, we achieved the similar estimation of exchange coupling field as well as obtained through the ZSHE measurements.

In summary, we report the investigation of MPE between monolayer graphene and 2D ferromagnet CrBr₃, which results in a considerable Zeeman splitting field

in graphene. The MPE effect shown in our graphene/CrBr₃ van der Waals heterostructures therefore not only reveal the origin and prediction of magnetic exchange field at the interface of 2D van der Waals heterostructures, but also guide the design of next-generation 2D spin logic and memory devices via effect control of local spin generation and modulation.

Chapter 4

Nonreciprocal charge transport in MnBi_2Te_4

Antiferromagnetic materials have attracted lots of attentions in the past decade[38]. Owing to the robust magnetic order, intrinsic high antiferromagnetic dynamic frequency and vanishing stray field, antiferromagnetic spintronic devices show potential applications in signal processing, data storage and high-speed computing. In some application areas, antiferromagnetic materials show better performances than that of the ferromagnetic materials[39].

Nonreciprocal charge transport phenomena have been intensively studied in lots of systems, such as p-n junctions, magnetic bilayers[52], topological insulators[53] and chiral magnets[54], etc. The nonreciprocal charge transport not only reveals the fundamental symmetry breaking, but also paves ways to applications, such as rectification.

Here, we studied the nonreciprocal charge transport properties in layered MnBi_2Te_2 (MBT). We also demonstrated that the nonreciprocal charge transport is gate tunable. The observed gate tunable nonreciprocal charge transport might pave ways to applications of antiferromagnetic spintronics.

4.1 Introduction

4.1.1 Onsager reciprocal theorem

In the thermodynamic limit of a many-body system, the dissipative process determines the direction of the time because it's irreversible[55]. Onsager points out that time-reversal symmetry plays an important role in the macroscopic response functions linear to the external stimuli. For output A and input B with wavevector q and frequency ω , the Kubo formula satisfies the following relation:

$$K_{AB}(q, \omega, B) = \epsilon_A \epsilon_B K_{BA}(-q, \omega, -B) \quad (4.1)$$

where $\epsilon_A = \pm 1$ and $\epsilon_B = \pm 1$ corresponds to the even-odd case of the quantity A or B for time-reversal operator. Applying the Onsager's reciprocal theorem to the conductivity tensor, we obtain:

$$\sigma_{\alpha\beta}(q, \omega, B) = \sigma_{\beta\alpha}(-q, \omega, -B) \quad (4.2)$$

In systems with breaking inversion symmetry, the nonreciprocal charge transport is characterized by the directional current-voltage characteristics[56]. The wave vector q is replaced by current I , and the resistance R of the system is expressed by:

$$R = R_0[1 + \beta B^2 + \gamma BI] \quad (4.3)$$

The formula shows the resistance depends on the current direction and the broken time-reversal symmetry is needed. In this case, the nonlinear response is not constrained by the Onsager symmetry.

4.1.2 MnBi_2Te_4 : layered Chern insulator and Axion insulator

MnBi_2Te_4 is an A-type antiferromagnet, where each Mn^{2+} ion contributes magnetic moment of $5\mu_B$. The magnetic moment of the Mn^{2+} is ferromagnetically aligned within the septuple layer, but antiferromagnetically aligned between two adjacent layers. The intrinsic combination of magnetism and topology makes MnBi_2Te_4 an interesting platform to study fundamental physics and device applications.

Knowing the band structure is crucial to understand physical properties of this material. In 2019, two groups independently reported the gaped band structure of MnBi_2Te_4 investigated by angle-resolved photoemission spectroscopy (ARPES)[15, 57]. They observed that a structure in the surface electron bands, known as a Dirac cone, is modified near and below the temperature at which the material becomes antiferromagnetic, as shown in Figure 4.1a and b. However, several groups reported

FIGURE 4.1: ARPES results of the single crystal MnBi_2Te_4 . (a) A gaped band structure of MnBi_2Te_4 studied by ARPES. (b) Temperature dependent gap energy and magnetization, indicating the sample becomes gapless when the temperature is higher than the Néel temperature. (c) ARPES results that show gapless Dirac cone at 10K. Adapted from Reference [15, 16] with permission.

different results [16]. The previously observed surface gap was proved to be bulk gap, which has clear k_z dispersion. As shown in Figure 4.1c, ARPES results with linearly dispersed Dirac cone were observed at 10K with photon energy of 6.3 eV, which means the surface is gapless. The reported gapless Dirac cone was ascribed to the surface mediated reconstruction of the magnetic moments that differ from the bulk. The gapless Dirac cone indicates it hosts massless Dirac quasiparticles. Apart from ARPES results that show the band structure of single crystal MnBi_2Te_4 ,

FIGURE 4.2: RMCD results of different layer-number MnBi_2Te_4 . The spin flip transition was revealed by the sharp increase or decrease of the RMCD. After the spin flop transitions, all magnetic moments were aligned in the same direction. The spin flip and spin flop transition show clear even-odd layer dependence. Adapted from Reference [17] with permission.

the layer dependent magnetism was reported. The optical reflective magnetic circular dichroism revealed the intralayer ferromagnetic coupling and the interlayer antiferromagnetic coupling as shown in Figure 4.2[17, 58]. Though the antiferromagnetic coupling between two neighboring layers indicates vanishing net magnetization in even-layer MnBi_2Te_4 at zero external magnetic field, RMCD results shown in Figure 4.2 are not zero. This might be ascribed to the surface induced magnetism. The spin-flip field and spin-flop field of even-odd layer show oscillations, which is explained by the antiferromagnetic linear chain model.

FIGURE 4.3: Quantum anomalous Hall effect in MnBi_2Te_4 . (a) and (b) shows the QAH in 7-SL MnBi_2Te_4 . (c) and (d) shows the high Chern number quantum anomalous Hall effect under high magnetic field. Adapted from Reference [18] with permission.

Electrical transport experiments demonstrated unambiguous evidence that MnBi_2Te_4 is a Chern insulator with layer-number tunable Chern number [18, 59]. As shown in Figure 4.3 a and b, in a 7-SL MnBi_2Te_4 , the Hall resistance R_{yx} was quantized with Chern number of -1 under high magnetic field, and the longitudinal resistance R_{xx} becomes very small. The magnetic field dependence clearly indicated the development of the dissipationless chiral edge channels, confirming that MnBi_2Te_4 is a Chern insulator. Wang Group reported high Chern number quantum anomalous Hall effect in a ten-layer MnBi_2Te_4 with Chern number of -2 at high magnetic field as shown in Figure 4.3.

Even layer MnBi_2Te_4 also hosts the axion insulator phase [19, 20]. The axion insulator is an exotic topological phase, which hosts zero Chern number but a nonzero

FIGURE 4.4: Axion insulator phase in 6-SL MnBi_2Te_4 . (a) Temperature dependent Hall resistance R_{yx} and longitudinal resistance R_{xx} . The axion phase at zero magnetic field shows a vanishing R_{yx} and a very large R_{xx} . Turning on the magnetic field, a phase transition from axion phase to quantum anomalous Hall phase occurred. (b) The axion field $E \cdot B$ was used to tune the Berry curvature and therefore the layer Hall effect. Adapted from Reference [19, 20] with permission.

topological Chern-Simons term. Traditional method to build an axion insulator is to fabricate quantum anomalous Hall heterostructures with different coercive field. MnBi_2Te_4 possesses intrinsically antiferromagnetic coupling between two neighbouring layers, which provides an excellent platform to study axion physics. Yayu group reported the robust axion phase in a 6-SL MnBi_2Te_4 at zero magnetic field. A phase transition from axion insulator to Chern insulator happened while turning on the magnetic field. Suyang group demonstrated axion field $E \cdot B$ manipulation of the layer Hall effect in a 6-SL MnBi_2Te_4 as shown in Figure 4.4.

4.2 Method

Since MBT is very difficult to obtain thin layers by conventional methods, we adopt the Al_2O_3 assisted method to fabricate thin-layer MBT[59]. First, we obtain thick

flakes on the tape by exfoliation from bulk crystal. Then we cover the tape with Al_2O_3 thin film deposited by thermal evaporation. The deposition was performed at the oxygen environment. After the deposition of Al_2O_3 thin film, we used thermal release tapes to pick up the Al_2O_3 with MBT flakes. Then, the Al_2O_3 /MBT was released onto the polydimethylsiloxane (PDMS). Next, we used an optical microscope to choose thin flakes on the PDMS. The thickness of the obtained thin MBT flake was determined by the optical contrast as shown in Figure 4.5. The optical image's green channel was used to obtain the reflection intensity. The optical contrast is determined by $(G^{\text{R}}_{\text{sample}} - G^{\text{R}}_{\text{substrate}}) / G^{\text{R}}_{\text{substrate}}$, where $G^{\text{R}}_{\text{sample}}$ and $G^{\text{R}}_{\text{substrate}}$ are reflection intensity of sample and Al_2O_3 substrate, respectively. All these process were performed in a Nitrogen filled glove box.

FIGURE 4.5: Determining the thickness of MBT thin flakes. (a) Optical image of the MBT/ Al_2O_3 on the PDMS. The layer number is labeled. (b) Optical contrast as a function of the layer number.

After determining the layer number, We transferred the Al_2O_3 /MBT from PDMS onto the Si/SiO₂ substrate. To protect the sample and avoid degradation in the electrode fabrication process, we did not use electron-beam lithography(EBL) to develop patterns. Instead, we used stencil mask to fabricate electrical contacts.

We used Cr/Au with thickness of 10nm/100nm as metal electrodes. The optical image of the fabricated 5-SL MnBi_2Te_4 is shown in Figure 4.6. To protect the device during transferring from glove box into the cryostation, we covered a hBN flake on the sample. The back gate voltage was applied by Si/SiO₂. For samples with top gate, we covered a graphite as electrode and the covered hBN was used as dielectric layer.

FIGURE 4.6: Optical image of the 5-SL MnBi_2Te_4 device.

4.3 Field induced Quantum anomalous Hall effect in MBT

First, we show the dissipationless edge state when the quantum anomalous Hall is developed at a low temperature and high magnetic field. Figure 4.7a shows the

crystal structure of the MBT. Our device is consisted of a 5-SL MBT with the Néel temperature of around 23 K. Figure 4.7b shows the resistance-temperature curve, in which the resistance peak indicates the antiferromagnet-paramagnet phase transition. To reveal the QAH in MBT, we applied a gate voltage of 22 V and tuned the Fermi level lying in the energy gap. The odd-layer MBT shows an uncompensated magnetism under zero external magnetic field as the temperature is below the Néel temperature, as shown in Figure 4.7c. Increasing the magnetic field up to 7 T, we observed the magnetic field induced quantum anomalous Hall effect with the R_{xy} value approaching to 0.977 h/e^2 at 1.650 K. At the same time, the R_{xx} value reaches to 0.019 h/e^2 , indicating dissipationless transport when the QAH is developed as shown in Figure 4.7d. We didn't observe the QAH under zero external magnetic field and we attributed this to the large disorder and negligible exchange gap without external magnetic field. Increasing the temperature leads to the breakdown of the QAH, manifesting as increased R_{xx} and decreased R_{xy} , in which the dissipative conducting channels developed due to thermal excitation. Measuring the temperature dependent magnetoresistance also revealed the energy gap for developing QAH. In Figure 4.7e, by fitting the Arrhenius plot of $\ln(R_{xx})$ as a function of $1/T$ at 7 T, we extracted the energy gap of 0.944 meV. We noted the hysteresis vanished at the temperature of 23 K, which was consistent with the Néel temperature. All electrical transport measurements are performed in a helium bath cryostat. The cryostat is equipped with a superconducting magnet. The maximum magnetic field in the out-of-plane direction is $\pm 7 \text{ T}$ and in the in-plane direction is $\pm 1 \text{ T}$. The temperature is ranging from 1.65 K to 300 K. The gate voltage is

FIGURE 4.7: Field induced quantum anomalous Hall effect in MnBi_2Te_4 . (a) shows the crystal structure of the MnBi_2Te_4 . (b) shows the resistance as a function of the temperature, in which the peak around 23K corresponds the Néel temperature. (c) and (d) show the anomalous Hall effect and the longitudinal magnetoresistance at different temperatures. The gate voltage is set to be 22V and the Fermi level locates in the energy gap. The quantized R_{xy} and almost vanishing R_{xx} indicate the field induced quantum anomalous Hall phase. (d) shows the energy gap obtained by fitting the Arrhenius plot of $\ln(R_{xx})$ as a function of $1/T$ at 7 T.

applied by a Keithely 2636B Source-Meter. The first and second order voltage is measured by SR-830 lock-in amplifier and Zurich MFLI lock-in amplifier.

4.4 Non-reciprocal charge transport in MBT

Next, we studied the nonreciprocal charge transport of the 5-SL MBT device. Figure 4.8a shows the measurement scheme. We injected 1uA RMS AC current to the device, and the frequency of the AC current was set as 17.777Hz. The 35.554 Hz longitudinal voltage was detected by the phase sensitive lock-in amplifier. In

this measurement scheme, the voltage can be written as:

$$V_{xx} = \sqrt{2}i \sin(\omega t) R_{xx} = \sqrt{2}i \sin(\omega t) R_0 + \gamma R_0 \hat{M} i^2 (1 - \cos(2\omega t)) \quad (4.4)$$

where R_0 is the resistance that does not change with the current, γ is the constant that is proportional to the strength of the nonreciprocal charge effect, and $\hat{M}(\pm 1)$ is the magnetization direction of MBT. As indicated by Equation (4.3), the nonreciprocity arising from the external magnetic field leads to a nonlinear current-voltage characteristic, and therefore the second harmonic signals can be used to probe the nonreciprocity. The measured second order longitudinal voltage reveals the value of γ .

In Figure 4.8b and c, we plotted the second harmonic longitudinal resistance as a function of current. To show the intrinsic behaviour of the second order resistance, we antisymmetrized the $R_{L/R}^{2\omega}$. The R-H loop exhibits several kinks that indicate the phase transition between different magnetic states, which is in agreement with the first order Hall measurements. Sweeping the magnetic field from -7 T to -5 T, all spins are polarized at state $\downarrow\downarrow\downarrow\downarrow$, and $R_L^{2\omega}$ shows a plateau at this state. While sweeping the magnetic field from -5 T to -3 T, the MBT device undergoes a spin flop transition with $\downarrow\downarrow\downarrow \rightarrow \leftarrow$ state to $\downarrow\downarrow\downarrow\uparrow\uparrow$. Further sweeping the magnetic field to the positive direction from -3 T to 0 T, it follows transition from $\downarrow \rightarrow \leftarrow \uparrow\downarrow$ to $\downarrow\uparrow\downarrow\uparrow\downarrow$. Owing to the different net magnetization at the spin $\downarrow\uparrow\downarrow\uparrow\downarrow$ state and spin $\uparrow\downarrow\uparrow\downarrow\uparrow$ state, the $R_L^{2\omega}$ -H curves show hysteresis while sweeping from 7 T to -7 T.

We then measured $R_R^{2\omega} - H$ loops at the right edge of the MBT device shown in Figure 4.8. The $R_R^{2\omega} - H$ loop shows the opposite trend compared with that of the left

FIGURE 4.8: Nonreciprocal charge transport in MBT. (a) shows the measure scheme. The AC current with frequency of 17.777 Hz was sent to the device and the second order longitudinal resistance was measured by the phase sensitive lock-in amplifier. (b) and (c) show the second order longitudinal resistance as a function of the magnetic field for left and right edge.

edge. We first focus on the fully spin polarized state $\downarrow\downarrow\downarrow\downarrow$, where $R_L^{2\omega} - H$ shows a negative value while $R_R^{2\omega} - H$ shows a positive value. At the spin state $\uparrow\uparrow\uparrow\uparrow$, the behaviour of second order resistance reverses. At zero magnetic field, though QAH effect is not developed at low temperature due to disorders, the second order resistance measurements reveal opposite trends of the charge transport. The edge dependent behaviour strongly indicates that the nonreciprocal charge transport we observed in MBT is related to chiral edge states. Gate dependent measurements provide insight into the origin of the nonreciprocal charge transport effect in MBT. In Figure 4.9c, we showed the gate dependent R_{xx} and R_{xy} at 10 K, and found that

FIGURE 4.9: Gate dependent nonreciprocal charge transport in MBT. (a) shows the second order longitudinal resistance at different gate voltages of the left edge. (b) shows the second order longitudinal resistance at different gate voltages of the right edge. (c) The gate dependent R_{xx} and R_{xy} indicate the corresponding gate voltage when tuning the Fermi level into the energy gap. (d) shows the second order longitudinal resistance at 7 T as a function of gate voltage of the left edge. (e) shows the second order longitudinal resistance at 7 T as a function of gate voltage of the right edge.

the Fermi level lies in the energy gap when the gate voltage ranges from 22V to 28 V. Decreasing or increasing gate voltage tune the carrier type to hole or electron type respectively. At the left edge shown in Figure 4.9a, when we tuned the carrier type from hole to electron type, the second order resistance $R_L^{2\omega} - H$ at the spin state $\uparrow\uparrow\uparrow\uparrow$ was tuned from positive to negative, while at the spin state $\downarrow\downarrow\downarrow\downarrow$, the $R_L^{2\omega} - H$ was tuned from negative to positive. The $R_L^{2\omega}$ at zero magnetic field followed the same trend, which indicates it shares the same origin as that of the fully spin polarized state. At the right side shown in Figure 4.9b, we found the reversed

behaviour. We summarized the gate dependence of $R_L^{2\omega}$ and $R_R^{2\omega}$ at the fully spin polarized state $\uparrow\uparrow\uparrow\uparrow$ shown in Figure 4.9d and e. The $R_L^{2\omega}$ goes across the zero point at the gate voltage of 46 V while the $R_R^{2\omega}$ vanished at around 22 V. The difference for left edge and right edge might result from the ununiform doping in the device. Even though there is a difference at the two edge, the overall behaviours show opposite trends. We also showed the temperature dependent nonreciprocal charge transport in Figure 4.10. The hysteresis disappeared when the temperature was increased to 23K.

We then turn our attention to the physical mechanism for the observed nonrecipro-

FIGURE 4.10: Temperature dependent nonreciprocal charge transport in 5-layer MBT.

cal charge transport. To date, there are several scenarios to describe the nonreciprocal charge transport in magnetic materials and magnetic heterostructures[52, 60,

[61]. In heavy metal/ferromagnet heterostructures, the current induced spin orbit torque modifies the magnetization and therefore leads to different resistance with opposite current directions. Another possible reason is the asymmetric scattering of electrons by magnons due to the spin Hall effect at the interface of topological insulator/ferromagnet. Anomalous Nernst effect might also contribute to nonreciprocal charge transport due to the temperature gradient caused by ohmic heating effect. However, these models cannot explain the edge dependence observed in our experiments. We therefore adopt the skew scattering model that previously describe the nonreciprocal charge transport phenomena in QAHE ferromagnet[60]. The nonreciprocal charge transport was ascribed to the asymmetric backscattering of charge carriers at chiral edge. The longitudinal resistance is proportional to the scattering rate of the charge carriers. When the device is slightly doped, the chemical potential of one side of the edge is higher than that of the bulk, while the other side shows opposite relation. Therefore, charge carriers moving along the different edges are scattered differently, which leads to nonreciprocal charge transport in this quantum anomalous Hall system.

4.5 Conclusion

Here, we systematically studied the nonreciprocal charge transport in 5-SL MnBi_2Te_4 . The fabricated 5-SL MnBi_2Te_4 device shows a Néel temperature of 23K. The quantum anomalous Hall effect was observed at high magnetic field with Chern number

of -1. Nonreciprocal charge transport effect is studied by a phase sensitive lock-in technique and we show the edge dependent edge transport at 10K, where the asymmetric backscattering caused by the bulk states leads to directional resistance. Due to the finite net magnetization, the non reciprocal charge transport is observed at zero magnetic field. The gate dependence shows negative $R^{2\omega}$ to positive $R^{2\omega}$ transition at the left edge with -7T when the doping level was tuned from holes to electrons. At the right edge, this behaviour reverses, which is consistent with the chiral nature of the edge channel. Temperature dependence shows that the nonreciprocal charge transport hysteresis loops disappear when the temperature is above the Néel temperature.

Our study on nonreciprocal charge transport in 5-SL MnBi_2Te_4 helps to understand the chiral edge transport of the quantum anomalous Hall insulator. It also paves the way to build new electronic devices and inspires the studied in spintronics using two-dimensional van der Waals materials.

Chapter 5

Conclusions and Outlook

5.1 Conclusions

Two-dimensional van der Waals magnetic materials have shown their advantages in both fundamental studies and potential applications. Long range spin ordered system in two dimensions becomes realistic, which removes the restriction of the Mermin–Wagner theorem due to the magnetic anisotropy. The rich magnetic orders, for example, the ferromagnetic intralayer coupling and interlayer antiferromagnetic coupling, have been intensively studied. The coupling of magnetic order and crystal lattice leads to nonreciprocal second harmonic generation and Raman scattering. The intertwined magnetism and band topology lead to the quantum anomalous Hall and axion insulators. Meanwhile, new device applications built by two-dimensional van der Waals materials and their heterostructures have shown excellent performance, and exhibit potential applications in spintronics. Applications

of these materials may pave ways to next-generation high-performance computing and memory devices.

This thesis focuses on physical properties of the van der Waals magnetic materials, including CrBr_3 and MnBi_2Te_4 . With optical and electrical probing methods, ferromagnetism in layered CrBr_3 , nonreciprocal charge transport in MnBi_2Te_4 and magnetic proximity effect in $\text{CrBr}_3/\text{graphene}$ were uncovered. These studies will be helpful to understand the fundamental physics of the van der Waals magnetic materials, as well as inspire more research interests in device applications.

5.1.1 Ferromagnetism in atomically thin van der Waals

CrBr_3

Ferromagnetism in monolayer CrBr_3 was probed by polarization resolved photoluminescence (PL). The origin of the PL was ascribed to the localized d-d transition, which shows broad linewidth and linear power dependence. Selectively exciting and collecting circularly polarized light (σ^+ and σ^-), the PL intensity as a function of magnetic field exhibit hysteresis loops, indicating spontaneously developed magnetic moments, in other words, ferromagnetism. The coercive field and the Curie temperature were revealed. The layer-number dependent hysteresis loops show clear evidence that the interlayer coupling between two neighbouring layers are ferromagnetic. The study of atomically thin van der Waals magnet CrBr_3 paves the way to design new optoelectronic and spintronic devices.

5.1.2 Magnetic proximity effect in graphene/CrBr₃ heterostructures

Two-dimensional graphene/CrBr₃ heterostructures show strong magnetic proximity effect. The Zeeman spin Hall effect probed by non-local measurements clearly indicates the strong magnetic proximity effect. The strength of the magnetic proximity effect is estimated by measuring the Zeeman splitting field, which shows a significant magnetic proximity field even in a low magnetic field. More importantly, the anomalous longitudinal resistance at the Dirac point $R_{XX,D}$ is dependent on the magnetic field near $\nu = 0$, which is ascribed to the magnetic proximity induced new ground state phases. The observation of the magnetic proximity effect in graphene/CrBr₃ heterostructures reveals strong magnetic coupling between van der Waals materials and thus provides guidance for designing next-generation 2D spin logic and memory devices.

5.1.3 Nonreciprocal charge transport in magnetic topological insulator MnBi₂Te₄

Nonreciprocal charge transport was observed in 5-SL MnBi₂Te₄. Through the crystal structure is inversion symmetric, the backscattering of the charge carriers at chiral edge is asymmetric, leading to directional magnetoresistance. We used the Al₂O₃ assisted method to fabricate MnBi₂Te₄ thin flakes. After estimating the

thickness of the obtained MnBi_2Te_4 thin flakes by optical contrast, the 5-SL sample was selected. The metal electrodes were then fabricated by a stencil mask. The quantum anomalous Hall effect at high magnetic field was demonstrated, which confirmed the chiral edge channel. The second order magnetoresistance was used to study the nonreciprocal charge transport and the magnetic field dependence, which shows clear hysteresis loops due to the finite net magnetic moment at zero magnetic field. The gate voltage was used to tune the nonreciprocal charge transport, corresponding to differences between the scattering rate of electrons and holes. The study of nonreciprocal charge transport opens the door to develop new electronic devices using magnetic topological van der Waals materials.

5.2 Outlook

Investigations of magnetism in two dimensional van der Waals materials have shown rich physics and potential applications in electronics and spintronics. However, there are still lots of areas that researchers should pay attention on.

5.2.1 Orbital magnetism in Morié superlattice

Ferromagnetism has been observed in graphene and transition metal dichalcogenide Morié superlattice systems. The ferromagnetism has the orbital origin and topological nature. Robust Chern insulator phase was reported in twisted bilayer graphene[62] and AB stacking[21] $\text{MoTe}_2/\text{WSe}_2$ heterostructures as shown

in Figure 5.1. In two heterostructures, at low temperatures, well quantized Hall resistance R_{xy} and very small longitudinal resistance R_{xx} at zero magnetic field in electrical transport provided clear evidences of the Chern insulator phase. Electron correlation and topology play important roles to achieve Chern insulators in Morié superlattice. The observation of the quantum anomalous Hall effect in such

FIGURE 5.1: Quantum anomalous Hall effect in Morié superlattice. (a) and (b) Quantum anomalous Hall effect in MoTe₂/WSe₂ Morié heterostructure. (c) Temperature dependent R_{xx} and R_{xy} . The Curie temperature is around 6 K. (d) R_{xx} as a function of the magnetic field and filling factor. Adapted from Reference [21] with permission.

Morié superlattice might inspire researchers in quantum computing using van der Waals materials. For example, the combination of superconductivity and quantum anomalous Hall effect might be helpful to study Majorana fermion, which is a promising candidate for quantum qubit in topological quantum computing.

5.2.2 Van der Waals spintronics

Magnetic materials are key ingredients to develop spintronic devices, including magnetic tunneling junctions and magnetic sensors. To achieve high performance in spintronic devices, flat interfaces are highly demanded. Van der Waals materials have shown advantages in atomically flat interfaces between two layers, which are free from defects and lattice mismatch in traditional magnetic films. Therefore, building all vdW spintronic devices is promising to improve device performance, where atomically flat contact between two-dimensional vdW materials enables the devices to achieve uniform spin tunnelling. The main problem of the recently reported devices is that the working temperature is limited by the Curie temperature, and therefore it only works at a low temperature.

To overcome this problem, room-temperature van der Waals ferromagnets must be used. We are trying to grow new van der Waals materials to realize the goal. For example, chemical vapor deposition (CVD) grown Fe_5GeTe_2 with 280 K Curie temperature was demonstrated in [22]. As shown in Figure 5.2, ferromagnetic behaviours were revealed by RMCD and the spontaneous magnetization preserved at 280 K. Searching for high Curie-temperature van der Waals ferromagnets will shed light on all van der Waals spintronics.

FIGURE 5.2: Near room-temperature ferromagnetism in Fe_5GeTe_2 . (a) The top view of spin-polarized d electron localized on Fe atoms. The red and green color of density localized on Fe atom suggest opposite spin directions. (b) The optical image of the CVD-grown Fe_5GeTe_2 . The scale bar is $20\ \mu\text{m}$. (c) RMCD hysteresis loops of Fe_5GeTe_2 at different temperatures. The nonzero RMCD under zero magnetic field at 280 K indicated near room-temperature ferromagnetism. Adapted from Reference [22] with permission.

List of Author's Awards, Patents, and Publications¹

Journal Articles

- **Zhaowei Zhang***, Jingzhi Shang*, Chongyun Jiang*, Abdullah Rasmita, Weibo Gao, Ting Yu, “Direct photoluminescence probing of ferromagnetism in monolayer two-dimensional CrBr₃” *Nano Letters* 19 (5), 3138-3142.
- Govindan Kutty Rajendran Nair*, **Zhaowei Zhang***, Fuchen Hou*, Ali Abdelaziem*, Xiaodong Xu, Steve Wu Qing Yang, Nan Zhang, Weiqi Li, Chao Zhu, Yao Wu, Heng Weiling, Lixing Kang, Teddy Salim, Jiadong Zhou, Lin Ke, Junhao Lin, Xingji Li, Weibo Gao, Zheng Liu, “Phase-pure two-dimensional Fe_xGeTe₂ magnets with near-room-temperature T_C ” *Nano Research* 2021.
- Anyuan Gao, Yu-Fei Liu, Chaowei Hu, Jian-Xiang Qiu, Christian Tzschaschel, Barun Ghosh, Sheng-Chin Ho, Damien Bérubé, Rui Chen, Haipeng Sun, **Zhaowei Zhang**, Xin-Yue Zhang, Yu-Xuan Wang, Naizhou Wang, Zumeng

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Huang, Claudia Felser, Amit Agarwal, Thomas Ding, Hung-Ju Tien, Austin Akey, Jules Gardener, Bahadur Singh, Kenji Watanabe, Takashi Taniguchi, Kenneth S Burch, David C Bell, Brian B Zhou, Weibo Gao, Hai-Zhou Lu, Arun Bansil, Hsin Lin, Tay-Rong Chang, Liang Fu, Qiong Ma, Ni Ni, Su-Yang Xu, "Layer Hall effect in a 2D topological axion antiferromagnet" *Nature* 2021, 595, 7868, 521-525.

- Shen Lai, Huiying Liu, **Zhaowei Zhang**, Jianzhou Zhao, Xiaolong Feng, Naizhou Wang, Chaolong Tang, Yuanda Liu, KS Novoselov, Shengyuan A Yang, Wei-bo Gao, "Third-order nonlinear Hall effect induced by the Berry-connection polarizability tensor" *Nature Nanotechnology* 2021.
- Chaolong Tang, **Zhaowei Zhang**, Shen Lai, Qinghai Tan, Wei-bo Gao, "Magnetic Proximity Effect in Graphene/CrBr₃ van der Waals Heterostructures" *Advanced Materials* 32 (16), 1908498.
- Jiadong Zhou, Junhao Lin, Hunter Sims, Chongyun Jiang, Chunxiao Cong, John A Brehm, **Zhaowei Zhang**, Lin Niu, Yu Chen, Yao Zhou, Yanlong Wang, Fucui Liu, Chao Zhu, Ting Yu, Kazu Suenaga, Rohan Mishra, Sokrates T Pantelides, Zhen-Gang Zhu, Weibo Gao, Zheng Liu, Wu Zhou, "Synthesis of Co-Doped MoS₂ Monolayers with Enhanced Valley Splitting" *Advanced Materials* 32 (11), 1906536.

Bibliography

- [1] F Duncan M Haldane. Model for a quantum hall effect without landau levels: Condensed-matter realization of the” parity anomaly”. *Physical Review Letters*, 61(18):2015, 1988. [x](#), [19](#)
- [2] Bevin Huang, Genevieve Clark, Efrén Navarro-Moratalla, Dahlia R Klein, Ran Cheng, Kyle L Seyler, Ding Zhong, Emma Schmidgall, Michael A McGuire, David H Cobden, et al. Layer-dependent ferromagnetism in a van der waals crystal down to the monolayer limit. *Nature*, 546(7657):270–273, 2017. [x](#), [20](#), [21](#), [34](#)
- [3] Cheng Gong, Lin Li, Zhenglu Li, Huiwen Ji, Alex Stern, Yang Xia, Ting Cao, Wei Bao, Chenzhe Wang, Yuan Wang, et al. Discovery of intrinsic ferromagnetism in two-dimensional van der waals crystals. *Nature*, 546(7657):265–269, 2017. [x](#), [20](#), [21](#), [34](#)
- [4] Shengwei Jiang, Jie Shan, and Kin Fai Mak. Electric-field switching of two-dimensional van der waals magnets. *Nature Materials*, 17(5):406–410, 2018. [x](#), [22](#), [23](#), [34](#)
- [5] Shengwei Jiang, Lizhong Li, Zefang Wang, Kin Fai Mak, and Jie Shan. Controlling magnetism in 2d CrI_3 by electrostatic doping. *Nature Nanotechnology*, 13(7):549–553, 2018. [x](#), [22](#), [23](#)
- [6] Yujun Deng, Yijun Yu, Yichen Song, Jingzhao Zhang, Nai Zhou Wang, Zeyuan Sun, Yangfan Yi, Yi Zheng Wu, Shiwei Wu, Junyi Zhu, et al. Gate-tunable

- room-temperature ferromagnetism in two-dimensional Fe_3GeTe_2 . *Nature*, 563 (7729):94–99, 2018. [x](#), [20](#), [22](#), [23](#), [24](#), [34](#)
- [7] Zhe Wang, Ignacio Gutiérrez-Lezama, Nicolas Ubrig, Martin Kroner, Marco Gibertini, Takashi Taniguchi, Kenji Watanabe, Ataç Imamoğlu, Enrico Giannini, and Alberto F Morpurgo. Very large tunneling magnetoresistance in layered magnetic semiconductor CrI_3 . *Nature Communications*, 9(1):1–8, 2018. [xi](#), [25](#), [34](#)
- [8] Zhe Wang, Deepak Sapkota, Takashi Taniguchi, Kenji Watanabe, David Mandrus, and Alberto F Morpurgo. Tunneling spin valves based on $\text{Fe}_3\text{GeTe}_2/\text{hBN}/\text{Fe}_3\text{GeTe}_2$ van der waals heterostructures. *Nano Letters*, 18(7): 4303–4308, 2018. [xi](#), [25](#), [34](#)
- [9] John Cenker, Bevin Huang, Nishchay Suri, Pearl Thijssen, Aaron Miller, Tiancheng Song, Takashi Taniguchi, Kenji Watanabe, Michael A McGuire, Di Xiao, et al. Direct observation of two-dimensional magnons in atomically thin CrI_3 . *Nature Physics*, 17(1):20–25, 2021. [xi](#), [26](#), [27](#)
- [10] Xingzhi Wang, Jun Cao, Zhengguang Lu, Arielle Cohen, Hikari Kitadai, Tian-shu Li, Qishuo Tan, Matthew Wilson, Chun Hung Lui, Dmitry Smirnov, et al. Spin-induced linear polarization of photoluminescence in antiferromagnetic van der waals crystals. *Nature Materials*, pages 1–7, 2021. [xi](#), [28](#), [29](#)
- [11] Zhuoliang Ni, AV Haglund, H Wang, B Xu, C Bernhard, DG Mandrus, X Qian, EJ Mele, CL Kane, and Liang Wu. Imaging the néel vector switching in the monolayer antiferromagnet MnPS_3 with strain-controlled ising order. *Nature Nanotechnology*, pages 1–6, 2021. [xi](#), [28](#), [30](#)
- [12] Wenjin Zhao, Zaiyao Fei, Tiancheng Song, Han Kyou Choi, Tauno Palomaki, Bosong Sun, Paul Malinowski, Michael A McGuire, Jiun-Haw Chu, Xiaodong Xu, et al. Magnetic proximity and nonreciprocal current switching in a monolayer WTe_2 helical edge. *Nature Materials*, 19(5):503–507, 2020. [xi](#), [30](#), [31](#)

-
- [13] Kyle L Seyler, Ding Zhong, Dahlia R Klein, Shiyuan Gao, Xiaou Zhang, Bevin Huang, Efrén Navarro-Moratalla, Li Yang, David H Cobden, Michael A McGuire, et al. Ligand-field helical luminescence in a 2d ferromagnetic insulator. *Nature Physics*, 14(3):277–281, 2018. [xi](#), [35](#)
- [14] Zhiyong Wang, Chi Tang, Raymond Sachs, Yafis Barlas, and Jing Shi. Proximity-induced ferromagnetism in graphene revealed by the anomalous hall effect. *Physical Review Letters*, 114(1):016603, 2015. [xiii](#), [56](#)
- [15] Emile DL Rienks, Sebastian Wimmer, Jaime Sánchez-Barriga, Ondřej Čáha, Partha Sarathi Mandal, Jiří Ržíčka, Andreas Ney, Hubert Steiner, Valentine V Volobuev, Heiko Groiß, et al. Large magnetic gap at the dirac point in $\text{bi}_2\text{te}_3/\text{mnbi}_2\text{te}_4$ heterostructures. *Nature*, 576(7787):423–428, 2019. [xv](#), [73](#), [74](#)
- [16] Yu-Jie Hao, Pengfei Liu, Yue Feng, Xiao-Ming Ma, Eike F Schwier, Masashi Arita, Shiv Kumar, Chaowei Hu, Meng Zeng, Yuan Wang, et al. Gapless surface dirac cone in antiferromagnetic topological insulator mnbi_2te_4 . *Physical Review X*, 9(4):041038, 2019. [xv](#), [74](#)
- [17] Shiqi Yang, Xiaolong Xu, Yaozheng Zhu, Ruirui Niu, Chunqiang Xu, Yuxuan Peng, Xing Cheng, Xionghui Jia, Yuan Huang, Xiaofeng Xu, et al. Odd-even layer-number effect and layer-dependent magnetic phase diagrams in mnbi_2te_4 . *Physical Review X*, 11(1):011003, 2021. [xv](#), [75](#)
- [18] Jun Ge, Yanzhao Liu, Jiaheng Li, Hao Li, Tianchuang Luo, Yang Wu, Yong Xu, and Jian Wang. High-chen-number and high-temperature quantum hall effect without landau levels. *National Science Review*, 7(8):1280–1287, 2020. [xv](#), [76](#)
- [19] Chang Liu, Yongchao Wang, Hao Li, Yang Wu, Yaixin Li, Jiaheng Li, Ke He, Yong Xu, Jinsong Zhang, and Yayu Wang. Robust axion insulator and chern insulator phases in a two-dimensional antiferromagnetic topological insulator. *Nature Materials*, 19(5):522–527, 2020. [xv](#), [32](#), [76](#), [77](#)

- [20] Anyuan Gao, Yu-Fei Liu, Chaowei Hu, Jian-Xiang Qiu, Christian Tzschaschel, Barun Ghosh, Sheng-Chin Ho, Damien Bérubé, Rui Chen, Haipeng Sun, et al. Layer hall effect in a 2d topological axion antiferromagnet. *Nature*, 595(7868): 521–525, 2021. [xv](#), [76](#), [77](#)
- [21] Tingxin Li, Shengwei Jiang, Bowen Shen, Yang Zhang, Lizhong Li, Trithep Devakul, Kenji Watanabe, Takashi Taniguchi, Liang Fu, Jie Shan, et al. Quantum anomalous hall effect from intertwined moiré bands. *arXiv preprint arXiv:2107.01796*, 2021. [xvi](#), [91](#), [92](#)
- [22] Govindan Kutty Rajendran Nair, Zhaowei Zhang, Fuchen Hou, Ali Abdelazizem, Xiaodong Xu, Steve Wu Qing Yang, Nan Zhang, Weiqi Li, Chao Zhu, Yao Wu, et al. Phase-pure two-dimensional fexgete2 magnets with near-room-temperature tc. *Nano Research*, pages 1–8, 2021. [xvi](#), [93](#), [94](#)
- [23] K v Klitzing, Gerhard Dorda, and Michael Pepper. New method for high-accuracy determination of the fine-structure constant based on quantized hall resistance. *Physical Review Letters*, 45(6):494, 1980. [15](#)
- [24] Cui-Zu Chang, Jinsong Zhang, Xiao Feng, Jie Shen, Zuocheng Zhang, Minghua Guo, Kang Li, Yunbo Ou, Pang Wei, Li-Li Wang, et al. Experimental observation of the quantum anomalous hall effect in a magnetic topological insulator. *Science*, 340(6129):167–170, 2013. [18](#), [30](#)
- [25] Zaiyao Fei, Bevin Huang, Paul Malinowski, Wenbo Wang, Tiancheng Song, Joshua Sanchez, Wang Yao, Di Xiao, Xiaoyang Zhu, Andrew F May, et al. Two-dimensional itinerant ferromagnetism in atomically thin Fe_3GeTe_2 . *Nature Materials*, 17(9):778–782, 2018. [20](#), [52](#)
- [26] N David Mermin and Herbert Wagner. Absence of ferromagnetism or antiferromagnetism in one-or two-dimensional isotropic heisenberg models. *Physical Review Letters*, 17(22):1133, 1966. [20](#)
- [27] Cheng Gong and Xiang Zhang. Two-dimensional magnetic crystals and emergent heterostructure devices. *Science*, 363(6428), 2019. [22](#), [34](#), [54](#), [55](#)

-
- [28] Bevin Huang, Genevieve Clark, Dahlia R Klein, David MacNeill, Efrén Navarro-Moratalla, Kyle L Seyler, Nathan Wilson, Michael A McGuire, David H Cobden, Di Xiao, et al. Electrical control of 2d magnetism in bilayer CrI_3 . *Nature Nanotechnology*, 13(7):544–548, 2018. [22](#)
- [29] Tingxin Li, Shengwei Jiang, Nikhil Sivadas, Zefang Wang, Yang Xu, Daniel Weber, Joshua E Goldberger, Kenji Watanabe, Takashi Taniguchi, Craig J Fennie, et al. Pressure-controlled interlayer magnetism in atomically thin CrI_3 . *Nature Materials*, 18(12):1303–1308, 2019. [22](#)
- [30] Tiancheng Song, Zaiyao Fei, Matthew Yankowitz, Zhong Lin, Qianni Jiang, Kyle Hwangbo, Qi Zhang, Bosong Sun, Takashi Taniguchi, Kenji Watanabe, et al. Switching 2d magnetic states via pressure tuning of layer stacking. *Nature Materials*, 18(12):1298–1302, 2019. [22](#)
- [31] Bo Liu, Shanshan Liu, Long Yang, Zhendong Chen, Enze Zhang, Zihan Li, Jing Wu, Xuezhong Ruan, Faxian Xiu, Wenqing Liu, et al. Light-tunable ferromagnetism in atomically thin Fe_3GeTe_2 driven by femtosecond laser pulse. *Physical Review Letters*, 125(26):267205, 2020. [22](#)
- [32] Weijong Chen, Zeyuan Sun, Zhongjie Wang, Lehua Gu, Xiaodong Xu, Shiwei Wu, and Chunlei Gao. Direct observation of van der waals stacking-dependent interlayer magnetism. *Science*, 366(6468):983–987, 2019. [22](#), [26](#), [34](#)
- [33] Mohammed Alghamdi, Mark Lohmann, Junxue Li, Palani R Jothi, Qiming Shao, Mohammed Aldosary, Tang Su, Boniface PT Fokwa, and Jing Shi. Highly efficient spin-orbit torque and switching of layered ferromagnet Fe_3GeTe_2 . *Nano Letters*, 19(7):4400–4405, 2019. [24](#)
- [34] Xiao Wang, Jian Tang, Xiuxin Xia, Congli He, Junwei Zhang, Yizhou Liu, Caihua Wan, Chi Fang, Chenyang Guo, Wenlong Yang, et al. Current-driven magnetization switching in a van der waals ferromagnet Fe_3GeTe_2 . *Science Advances*, 5(8):eaaw8904, 2019. [24](#)

- [35] Tiancheng Song, Xinghan Cai, Matisse Wei-Yuan Tu, Xiaouu Zhang, Bevin Huang, Nathan P Wilson, Kyle L Seyler, Lin Zhu, Takashi Taniguchi, Kenji Watanabe, et al. Giant tunneling magnetoresistance in spin-filter van der waals heterostructures. *Science*, 360(6394):1214–1218, 2018. [25](#), [34](#)
- [36] Dahlia R Klein, David MacNeill, Jose L Lado, David Soriano, Efrén Navarro-Moratalla, Kenji Watanabe, Takashi Taniguchi, Soham Manni, Paul Canfield, Joaquín Fernández-Rossier, et al. Probing magnetism in 2d van der waals crystalline insulators via electron tunneling. *Science*, 360(6394):1218–1222, 2018. [25](#), [34](#)
- [37] Zeyuan Sun, Yangfan Yi, Tiancheng Song, Genevieve Clark, Bevin Huang, Yuwei Shan, Shuang Wu, Di Huang, Chunlei Gao, Zhanghai Chen, et al. Giant nonreciprocal second-harmonic generation from antiferromagnetic bilayer crig. *Nature*, 572(7770):497–501, 2019. [26](#), [35](#)
- [38] V Baltz, Aurelien Manchon, M Tsoi, T Moriyama, T Ono, and Y Tserkovnyak. Antiferromagnetic spintronics. *Reviews of Modern Physics*, 90(1):015005, 2018. [28](#), [71](#)
- [39] Tomas Jungwirth, X Marti, P Wadley, and J Wunderlich. Antiferromagnetic spintronics. *Nature Nanotechnology*, 11(3):231–241, 2016. [28](#), [71](#)
- [40] Sergey S Pershoguba, Saikat Banerjee, JC Lashley, Jihwey Park, Hans Ågren, Gabriel Aeppli, and Alexander V Balatsky. Dirac magnons in honeycomb ferromagnets. *Physical Review X*, 8(1):011010, 2018. [34](#), [36](#)
- [41] Qian Li, Mengmeng Yang, Cheng Gong, Rajesh V Chopdekar, Alpha T N’Diaye, John Turner, Gong Chen, Andreas Scholl, Padraic Shafer, Elke Arenholz, et al. Patterning-induced ferromagnetism of Fe_3GeTe_2 van der waals materials beyond room temperature. *Nano Letters*, 18(9):5974–5980, 2018. [34](#)
- [42] Minsoo Kim, Piranavan Kumaravadivel, John Birkbeck, Wenjun Kuang, Shuigang G Xu, DG Hopkinson, Johannes Knolle, Paul A McClarty,

- AI Berdyugin, M Ben Shalom, et al. Micromagnetometry of two-dimensional ferromagnets. *Nature Electronics*, 2(10):457–463, 2019. [34](#)
- [43] Bevin Huang, John Cenker, Xiaouu Zhang, Essance L Ray, Tiancheng Song, Takashi Taniguchi, Kenji Watanabe, Michael A McGuire, Di Xiao, and Xiaodong Xu. Tuning inelastic light scattering via symmetry control in the two-dimensional magnet CrI_3 . *Nature Nanotechnology*, 15(3):212–216, 2020. [34](#)
- [44] JF Dillon Jr, H Kamimura, and JP Remeika. Magneto-optical properties of ferromagnetic chromium trihalides. *Journal of Physics and Chemistry of Solids*, 27(9):1531–1549, 1966. [36](#)
- [45] Hongbo Wang, Fengren Fan, Shasha Zhu, and Hua Wu. Doping enhanced ferromagnetism and induced half-metallicity in CrI_3 monolayer. *EPL (Europhysics Letters)*, 114(4):47001, 2016. [42](#)
- [46] Jose L Lado and Joaquín Fernández-Rossier. On the origin of magnetic anisotropy in two dimensional CrI_3 . *2D Materials*, 4(3):035002, 2017. [49](#)
- [47] B Kuhlow and M Lambeck. Magnetic domain structures in CrBr_3 . *Physica B+C*, 80(1-4):365–373, 1975. [52](#)
- [48] Xiaoyang Lin, Wei Yang, Kang L Wang, and Weisheng Zhao. Two-dimensional spintronics for low-power electronics. *Nature Electronics*, 2(7):274–283, 2019. [54](#), [55](#)
- [49] Ivan J Vera-Marun, Vishal Ranjan, and Bart J Van Wees. Nonlinear detection of spin currents in graphene with non-magnetic electrodes. *Nature Physics*, 8(4):313–316, 2012. [55](#)
- [50] Hong-Xin Yang, A Hallal, D Terrade, Xavier Waintal, Stephan Roche, and Mairbek Chshiev. Proximity effects induced in graphene by magnetic insulators: First-principles calculations on spin filtering and exchange-splitting gaps. *Physical Review Letters*, 110(4):046603, 2013. [56](#)

- [51] Peng Wei, Sunwoo Lee, Florian Lemaitre, Lucas Pinel, Davide Cutaia, Wujoon Cha, Ferhat Katmis, Yu Zhu, Donald Heiman, James Hone, et al. Strong interfacial exchange field in the graphene/eu heterostructure. *Nature materials*, 15(7):711–716, 2016. [64](#)
- [52] Can Onur Avcı, Kevin Garello, Abhijit Ghosh, Mihai Gabureac, Santos F Alvarado, and Pietro Gambardella. Unidirectional spin hall magnetoresistance in ferromagnet/normal metal bilayers. *Nature Physics*, 11(7):570–575, 2015. [71](#), [85](#)
- [53] T Ideue, K Hamamoto, S Koshikawa, M Ezawa, S Shimizu, Y Kaneko, Y Tokura, N Nagaosa, and Y Iwasa. Bulk rectification effect in a polar semiconductor. *Nature Physics*, 13(6):578–583, 2017. [71](#)
- [54] K Ishizaka, MS Bahramy, H Murakawa, M Sakano, T Shimojima, T Sonobe, K Koizumi, S Shin, H Miyahara, A Kimura, et al. Giant rashba-type spin splitting in bulk bte. *Nature Materials*, 10(7):521–526, 2011. [71](#)
- [55] Lars Onsager. Reciprocal relations in irreversible processes. i. *Physical Review*, 37(4):405, 1931. [72](#)
- [56] GLJA Rikken, J Fölling, and P Wyder. Electrical magnetochiral anisotropy. *Physical Review Letters*, 87(23):236602, 2001. [73](#)
- [57] Mikhail M Otrokov, Ilya I Klimovskikh, Hendrik Bentmann, D Estyunin, Alexander Zeugner, Ziya S Aliev, S Gaß, AUB Wolter, AV Koroleva, Alexander M Shikin, et al. Prediction and observation of an antiferromagnetic topological insulator. *Nature*, 576(7787):416–422, 2019. [73](#)
- [58] Dmitry Ovchinnikov, Xiong Huang, Zhong Lin, Zaiyao Fei, Jiaqi Cai, Tiancheng Song, Minhao He, Qianni Jiang, Chong Wang, Hao Li, et al. Intertwined topological and magnetic orders in atomically thin chern insulator mnbi_2te_4 . *Nano Letters*, 21(6):2544–2550, 2021. [75](#)
- [59] Yujun Deng, Yijun Yu, Meng Zhu Shi, Zhongxun Guo, Zihan Xu, Jing Wang, Xian Hui Chen, and Yuanbo Zhang. Quantum anomalous hall effect in intrinsic

- magnetic topological insulator mnbi_2te_4 . *Science*, 367(6480):895–900, 2020. [76](#), [77](#)
- [60] Kenji Yasuda, Atsushi Tsukazaki, Ryutaro Yoshimi, KS Takahashi, Masashi Kawasaki, and Yoshinori Tokura. Large unidirectional magnetoresistance in a magnetic topological insulator. *Physical Review Letters*, 117(12):127202, 2016. [85](#), [86](#)
- [61] Yabin Fan, Qiming Shao, Lei Pan, Xiaoyu Che, Qinglin He, Gen Yin, Cheng Zheng, Guoqiang Yu, Tianxiao Nie, Massoud R Masir, et al. Unidirectional magneto-resistance in modulation-doped magnetic topological insulators. *Nano Letters*, 19(2):692–698, 2019. [86](#)
- [62] M Serlin, CL Tschirhart, H Polshyn, Y Zhang, J Zhu, K Watanabe, T Taniguchi, L Balents, and AF Young. Intrinsic quantized anomalous hall effect in a moiré heterostructure. *Science*, 367(6480):900–903, 2020. [91](#)