Evolution of interlayer and intralayer magnetism in three atomically thin chromium trihalides

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We conduct a comprehensive study of three different magnetic semiconductors, CrI₃, CrBr₃, and CrCl₃, by incorporating both few-layer and bilayer samples in van der Waals tunnel junctions. We find that the interlayer magnetic ordering, exchange gap, magnetic anisotropy, and magnon excitations evolve systematically with changing halogen atom. By fitting to a spin wave theory that accounts for nearest-neighbor exchange interactions, we are able to further determine a simple spin Hamiltonian describing all three systems. These results extend the 2D magnetism platform to Ising, Heisenberg, and XY spin classes in a single material family. Using magneto-optical measurements, we additionally demonstrate that ferromagnetism can be stabilized down to monolayer in more isotropic CrBr₃, with transition temperature still close to that of the bulk.

2D magnetism | chromium trihalides | tunneling spectroscopy

The recent discoveries of magnetism in the monolayer limit have opened a new avenue for 2D materials research (1–4). Already, several groups have reported a giant tunnel magnetoresistance effect across ultrathin CrI₃ layers (5–8) as well as electric field control of their magnetic properties (9–14). As with CrI₃, the entire family of magnetic chromium trihalides (CrX₃, X = Cl, Br, and I) possesses a layered structure together with relatively strong (weak) in-plane (out-of-plane) exchange coupling (15–20), prompting a thorough investigation of the interlayer and intralayer magnetic properties of all three materials in the 2D limit.

Within the layers, all three bulk compounds exhibit ferromagnetic (FM) order, although the easy axis is out-of-plane for CrI₃ and CrBr₃ and in-plane for CrCl₃. Interlayer magnetic interactions are not negligible, however, as CrI₃ (21) and CrBr₃ (22) are expected to exhibit FM ordering between the layers, while CrCl₃ (23) shows interlayer antiferromagnetic (AFM) order in the ground state. However, in ultrathin CrI₃ samples, spins in adjacent layers are, instead, AFM coupled, giving rise to giant tunnel magnetoresistance when all layers become unpolarized by a relatively small magnetic field (5–8). Due to the extreme sensitivity of tunnel magnetoresistance to interlayer magnetic order (5–8, 24, 25), we have fabricated graphite/CrX₃/graphite tunnel junctions that are fully encapsulated by hexagonal boron nitride (hBN). A schematic illustration of our devices is shown in Fig. 1*A*, and the detailed fabrication procedure can be found in *Methods*. In brief, we exfoliated CrX₃ within a nitrogen-filled glove box and stacked them between top and bottom graphite electrodes before encapsulation by hBN on both sides. Optical images of the devices are shown in *SI Appendix*, Fig. S1, and their current–voltage characteristics are shown in *SI Appendix*, Fig. S2.

We begin with temperature-dependent transport behavior under zero magnetic field. In Fig. 1*B*, we show junction resistance vs. temperature upon cooling for three representative devices

incorporating the three different trihalides. Their thicknesses measured by atomic force microscopy are CrI₃, 5.6 nm; CrBr₃, 5.2 nm; and CrCl₃, 9 nm. For easy comparison, the resistances have been normalized by their minimum and maximum values and range between 0 and 1. A marked kink is observed in all devices (CrI₃, 46 K; CrBr₃, 37 K; and CrCl₃, 17 K), close to their respective bulk magnetic transition temperatures [CrI₃, 61 K (21); CrBr₃, 37 K (22); and CrCl₃, 17 K (23)]. For magnetic tunnel barriers, it has been found that the resistance either decreases or increases abruptly below the critical temperature, depending on whether the magnetic ordering is FM or AFM, respectively (24–26). This is caused by a spin-filtering effect (24, 27), which effectively lowers (raises) the spin-dependent tunnel barrier upon exchange splitting in the FM (AFM) state. A schematic of this effect is shown in Fig. 1*B*, *Inset*. Our devices consist of layered magnetic semiconductors in a vertical transport geometry, and therefore we expect our measurements to be most sensitive to the interlayer magnetic ordering of the few-layer samples. We thus assert that CrCl₃ and CrI₃ exhibit interlayer AFM coupling in their ground state, while CrBr₃ shows interlayer FM coupling. For CrCl₃ and CrBr₃, this is consistent

Significance

Two-dimensional magnetic semiconductors such as CrI₃ are a new class of van der Waals material that may allow for the development of novel 2D spintronic devices. While strong magnetic anisotropy within the CrI₃ layers stabilizes ferromagnetism down to a monolayer, weak antiferromagnetic coupling between the layers gives rise to extremely large tunnel magnetoresistance. We use a combination of tunneling and magneto-optical measurements to investigate the entire 2D chromium trihalide family (CrX₃, X = I, Br, Cl). Our results elucidate both the interlayer coupling and intralayer spin Hamiltonian for all three materials, and further demonstrate that ferromagnetism can be stabilized in monolayer CrBr₃ and bilayer CrCl₃ without strong anisotropy.

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Fig. 1. Magnetic van der Waals tunnel junction incorporating ultrathin chromium trihalides. (A) Schematic illustration of the device. (B) Normalized temperature-dependent dc resistance of CrX_3 ($X = \text{I, Br, and Cl}$) at constant current of 0.1 nA. Insets show schematics of the spin-dependent tunnel barrier for AFM and FM interlayer coupling. Red and blue arrows indicate spin orientation and are used throughout.

with measurements of the bulk crystal, while those for CrI_3 indicate the opposite (FM coupling) (21).

We would like to understand whether the observed interlayer magnetic ordering persists down to the ultimate limit of two atomic layers; however, the resistance kink in the temperature dependence is less apparent for thinner samples, due to a smaller spin-filtering effect (*SI Appendix, Fig. S3*). We therefore turn to the magnetic field dependence. Here, ground-state AFM and FM ordering will yield different magnetoresistance behaviors. In Fig. 2, we show resistance vs. $B_{\perp}$ (field perpendicular to the layers) at several different temperatures for the three bilayer (2L) CrX_3 devices. In general, the tunneling resistance is smallest when spins in adjacent layers are parallel. First, for 2L CrI_3 at low temperature (Fig. 2A), the resistance decreases abruptly when the field exceeds ~ 0.75 T, indicating a spin-flip transition from the AFM ground state (antiparallel out-of-plane) to a parallel spin state at higher field. This resistance change decreases with increasing temperature until it completely disappears above the magnetic transition temperature. These observations are consistent with previous findings (5, 6). In comparison, the resistance of 2L CrCl_3 also decreases substantially with field (Fig. 2C), reflecting that the layers are AFM coupled at zero field. The resistance evolves continuously, however, as spins point in-plane in the ground state and gradually rotate with out-of-plane field. The easy axis of CrCl_3 will be characterized and discussed in more detail later (see Figs. 4 and 5). Finally, for 2L CrBr_3 , the low-temperature resistance is unchanged with field (Fig. 2B), since a spin-parallel FM state has naturally formed and states with both layers spin up or down would show no difference in resistance.

To confirm this scenario, we have further performed magnetic circular dichroism (MCD) measurements on another 2L CrBr_3 sample (Fig. 3A). Since the MCD signal is proportional to total out-of-plane magnetization, it can resolve the difference between these two spin states with degenerate resistance. The results taken at several different temperatures are shown in *SI Appendix, Fig. S4*. At low temperature, a finite magnetization is observed at zero field with hysteresis between field sweep up or down, corresponding to switching of the total spin direction of the FM coupled layers. In contrast, 2L CrI_3 shows no net magnetization at zero field as the layers are AFM coupled (1, 5, 9–11). The critical coercive field needed to flip the spin polarization is also much smaller for CrBr_3 (10 mT at 5 K). We have further performed MCD measurements on 1L, 3L, and 6L CrBr_3 and observed similar behavior (Fig. 3A and *SI Appendix, Fig. S4*). The temperature at which the hysteresis disappears is estimated to be 27, 36, and 37 K for 1L, 2L, and 3L, respectively. Interestingly, this transition temperature is not much decreased down to monolayer (Fig. 3B).

In addition to interlayer magnetic coupling, we would also like to understand the in-plane magnetic anisotropy of all three 2D

compounds in greater detail. We begin with comparing the difference in magnetoresistance behaviors between perpendicular and parallel field configurations for the few-layer devices at low temperature (Fig. 4A and C). For CrI_3 , the critical field needed to fully polarize all of the spins in-plane is 3 times larger than that out-of-plane ($B_{\parallel}^c = \sim 6.5$ T $\gg B_{\perp}^c = \sim 2$ T). In contrast, the out-of-plane critical field is slightly larger in CrCl_3 ($B_{\parallel}^c = \sim 2$ T $\lesssim B_{\perp}^c = \sim 2.4$ T). For CrBr_3 , however, magnetic anisotropy cannot be directly determined by magnetoresistance, since interlayer FM coupling results in nearly constant resistance independent of field orientation (*SI Appendix, Fig. S6*). Instead, we compared the MCD response of few-layer CrBr_3 for out-of-plane and in-plane field and obtained $B_{\parallel}^c = \sim 0.44$ T $\gg B_{\perp}^c = \sim 0.004$ T (Fig. 4B). Additional information about the layer dependence of the critical fields can be found in *SI Appendix, section IV*. These results clearly indicate that the magnetic anisotropy changes with changing halogen atom. We have further measured the full angular dependence of the tunneling current at 2 T for few-layer CrI_3 and CrCl_3 (Fig. 4A and C, Insets). Similar measurements for other magnetic field levels can be found in *SI Appendix, section V*. The results show that CrI_3 exhibits the behavior of a highly anisotropic, Ising-type spin system with out-of-plane easy axis. A 2 T field applied closely perpendicular to the layers fully polarizes the spins to establish a more conductive state, while the same field applied in-plane only slightly cants the spins to establish a small parallel component. While the easy axis of CrBr_3 is also out-of-plane, the system shows reduced anisotropy in comparison and is closer to Heisenberg. Finally, the easy axis of CrCl_3 is in-plane with small anisotropy—it requires a slightly smaller field to rotate the spins within the plane than it does to fully cant them perpendicular, which suggests a weak XY spin model.

These observed differences motivate a detailed microscopic understanding of the spin Hamiltonian for all three 2D systems, which can be extracted through observation of their excitations (magnons) at low junction biases. Toward this end, we have measured the ac conductance (dI/dV) vs. dc voltage V of all three 2L devices using standard lock-in methods (*SI Appendix, Fig. S10*). The conductance abruptly increases when the voltage reaches a magnon energy, due to the opening of an additional inelastic scattering channel (6, 28, 29). The magnon energies can then be seen as peaks in the $|d^2I/dV^2|$ spectrum. In Fig. 5A, we show, as a color plot, the evolution of $|d^2I/dV^2|$ vs. V with magnetic field along the hard axis for all three 2L trihalides, while similar data along the easy axis are shown in *SI Appendix, Fig. S11A*. In each case, at least two magnon modes can be seen dispersing with field. This is consistent with the underlying honeycomb lattice, which gives rise to two magnon energy branches in momentum space (17). The magnon density is largest at the M

Fig. 2. Tunneling probe of interlayer magnetic coupling in 2L CrX₃. Resistance vs. $B_{\perp}$ of (A) 2L CrI₃ taken at 10, 20, 30, 40, and 50 K, in sequence from blue to red; (B) 2L CrBr₃ at 1.4 K; and (C) 2L CrCl₃ at 1.4, 10, 20, 30, and 40 K, in sequence from blue to red.

point. The observation of additional peaks indicates that we are resolving magnons with different momenta.

The observed magnon energies can be largely understood by considering only the intralayer magnetic interaction within a single layer. To estimate the effect of interlayer coupling, we note that the easy axis critical field for both CrI₃ and CrCl₃ (~ 2 T for few-layer) decreases substantially with reduced thickness (*SI Appendix*, Fig. S5). In particular, it is ~ 0.1 T for 1L CrI₃ (1). This indicates that 2 T (or 0.2 meV for g factor = 2) is the energy required to overcome the interlayer AFM coupling for these materials. In contrast, $B_{\perp}^c$ maintains a small and nearly thickness-independent value for CrBr₃, which shows interlayer FM coupling. This energy scale is an order of magnitude smaller than the observed magnon energies, and so interlayer coupling should only play a perturbative role.

The minimal model to describe ferromagnetism in a single layer of CrX₃ is the 2D anisotropic Heisenberg model, described

by the Hamiltonian $H = -J \sum_{\langle i,j \rangle} (S_i^x S_j^x + S_i^y S_j^y + \alpha S_i^z S_j^z)$, where $S_{i(j)}^{x(y,z)}$

is the spin operator along the x (y , z) direction at the Cr³⁺ site i (j), J is the exchange coupling constant, α is the exchange anisotropy, and $\langle i,j \rangle$ denotes the approximation of the nearest-neighbor exchange coupling. By convention, z is chosen as the direction perpendicular to the layers and $J > 0$ for ferromagnetism. The application of a magnetic field contributes an additional Zeeman term $-g\mu_B B \sum_i S_i^z$ along the same spin direction.

We have performed a full spin wave analysis for monolayer CrX₃ based on the above Hamiltonian on the honeycomb lattice (*SI Appendix*, section VII). The results are shown in Fig. 5B and *SI Appendix*, Fig. S11B, and we now summarize. At zero field, the Γ and M point magnons have energies $\Gamma_{\pm} = (9/2)J(\alpha \pm 1)$ and $M_{\pm} = (3/2)J(3\alpha \pm 1)$. For α of order unity, $\Gamma_{-} \approx 0$ and $M_{+} \approx 2M_{-}$, restricting the magnon assignments in our data. For CrI₃ and CrCl₃, the most intense peaks are M_{+} and M_{-} modes, while the highest energy mode for CrBr₃ is assigned to be Γ_{+} , although M_{+} is also faintly visible for positive voltage. We note that, for CrI₃, this magnon assignment is consistent with a recent neutron scattering study of the bulk crystal (20), which shows comparable magnon energies (~ 9 and ~ 15 meV) at the M point. At other momenta, it may be important to also consider second and third nearest-neighbor terms in the spin Hamiltonian.

Fig. 3. MCD measurements on CrBr₃. (A) Low-temperature MCD vs. $B_{\perp}$ and (B) temperature-dependent normalized MCD at zero field [$MCD_{\perp}(T)/MCD_{\perp}(5K)$] for 1L, 2L, and 3L CrBr₃.

Table 1. Summary of magnetic properties of 2D CrX₃

	CrI ₃	CrBr ₃	CrCl ₃
Interlayer magnetic coupling	AFM	FM	AFM
T _C , K	Few L: 46 (tunneling) 2L: 45 (tunneling) 1L: 45 (MOKE) (1, 11)	Few L: 37 (tunneling) 3L: 37 (MCD) 2L: 36 (MCD) 1L: 27 (MCD)	Few L: 17 (tunneling) 2L: 16 (tunneling)
E _{ex} , meV	136	122	68
J, meV	2.29	1.56	0.92
α	1.04	1.01	0.99
Spin model	Ising	Anisotropic Heisenberg	Weak XY

that the M_± peak positions for CrI₃ do not shift at low fields. To account for the effect of interlayer coupling, we estimate the anisotropy field, B^a, for monolayer to be the difference between the critical fields applied along the hard and easy axes for the 2L devices (B^a = 3.63 T for CrI₃; B^a = 0.44 T for CrBr₃; and B^a = 0.23 T for CrCl₃). At high fields, all mode energies again increase by the Zeeman shift. The dashed lines in Fig. 5A and *SI Appendix, Fig. S11A* guide the eye to see this change. This simple model captures the essential features of the magnon positions and dispersions for all three compounds, indicating that the data can be largely understood by considering only nearest-neighbor interactions within a single layer.

Importantly, our analysis allows us to extract both the exchange energy *J* and exchange anisotropy *α* for the 2D trihalides. In Table 1, we have summarized these values together with other key properties measured in this work. The transition temperature *T_C*, *J*, and *α* all decrease with smaller halogen atom. We have further measured the low-temperature, exchange gap splitting of the band structure *E_{ex}* in few-layer samples (*SI Appendix, section VIII*), which shows a similar trend. The evolving anisotropy changes the 2D spin class from Ising (*α* > 1) in CrI₃ to anisotropic Heisenberg (*α* ≳ 1) in CrBr₃, and to weak XY (*α* ≲ 1) in CrCl₃. Surprisingly, the transition temperature is not substantially reduced down to 1L for CrBr₃ and 2L for CrCl₃, despite the low anisotropy in these materials, indicating that strong anisotropy is not necessary to stabilize magnetism in the 2D limit.

We now end by discussing two interesting implications of these results. First, we notice that the transition temperature for 2L CrBr₃ and CrCl₃ is already very near that of the bulk crystal, while that for few-layer CrI₃ (~46 K) is more reduced from the bulk transition temperature of 61 K. It is possible that changing interlayer magnetism from FM to AFM also modifies the transition temperature of this material. In contrast, thin CrBr₃ and CrCl₃ have similar interlayer coupling with their bulk counterparts. Second, the existence and/or nature of magnetism in monolayer CrCl₃ still remains an open question, as the 2D XY model is not expected to show long-range order at finite temperature. It may be possible that interlayer AFM coupling plays a nonnegligible role in stabilizing magnetism in 2Ls, although one cannot strictly rule out other more complex magnetic orders or the importance of additional in-plane exchange interactions beyond the nearest neighbor. Our work here paves the way for future studies on these topics.

Methods

Crystal Synthesis. The single crystals of CrX₃ (X = Cl and I) were grown by the chemical vapor transport method. The CrX₃ polycrystals were put into a silica tube with a length of 200 mm and inner diameter of 14 mm. The tube was evacuated down to 0.01 Pa and sealed under vacuum. The tubes were placed in a two-zone horizontal tube furnace, and the source and growth zones

were raised to 993 to 873 K and 823 to 723 K for 24 h, and then held there for 150 h. Shiny and plate-like crystals with lateral dimensions up to several millimeters can be obtained. To avoid degradation of CrX₃ crystals, the samples were stored in a glove box. The CrBr₃ single crystals were purchased from HQ Graphene.

Device Fabrication. Graphite (CoorsTek), h-BN (HQ Graphene), CrI₃, CrBr₃ (HQ Graphene), and CrCl₃ were exfoliated on polydimethylsiloxane-based gel (PF-40/17-X4 from Gel-Pak) within a nitrogen-filled glove box (*P_{O₂}*, *P_{H₂O}* < 0.1 ppm). Prepatterned Au (40 nm)/Ti (5 nm) electrodes were fabricated on 285-nm-thick SiO₂/Si by using conventional photolithography and lift-off methods, and e-beam deposition. Then, vertical heterostructures of hBN/graphite/CrX₃/graphite/hBN were sequentially stacked in a home-built transfer setup inside the glove box. The overlapping area of graphite/CrX₃/graphite was set to be ~10 μm²; 5.6- and 7-nm-thick CrI₃ (8 and 10 layers), 5.2- to 9-nm-thick CrBr₃ (8, 10, and 14 layers), and 6- to 9-nm-thick CrCl₃ (10, 12, and 15 layers) were used for fabrication. Thin graphite flakes were used as vertical contacts to the CrX₃ and connected to the prepatterned electrodes, while hBN flakes were used as a passivation barrier. Devices were annealed at 393 K in the glove box and were stored in a vacuum desiccator until the devices were loaded into a cryostat. For 2L CrX₃ devices, sequential pickup (30) was used for fabrication with ~1 μm² overlapping area.

Transport Measurements. Transport measurement was performed in either an He4 cryostat (base temperature 1.4 K) or an He3 cryostat (base temperature 0.3 K). The dc current/voltage measurements were performed with a Keithley 2450 source measure unit. The ac tunneling measurements were performed with an additional lock-in amplifier (Stanford Research Systems SR830 with 100-μV ac excitation and 77.77-Hz frequency). A piezo rotator (atto3DR) was used to rotate the sample relative to the magnetic field.

Magneto-Optical Measurements. The magnetization of hBN-encapsulated CrBr₃ flakes was characterized by the MCD microscopy in an He4 cryostat (AttoDry1000) with out-of-plane magnetic field. A diode laser at 405 nm with an optical power of 10 μW was focused to be a submicron spot size on the flakes by an objective of numerical aperture 0.8. The optical excitation was modulated by a photoelastic modulator at 50 kHz for left and right circular polarization. The laser reflected from CrBr₃ was collected by the same objective and then detected by a photodiode.

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