Layer-resolved magnetic proximity effect in van der Waals heterostructures

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Magnetic proximity effects are integral to manipulating spintronic1–4, superconducting5–8, excitonic9 and topological phenomena10–12 in heterostructures. These effects are highly sensitive to the interfacial electronic properties, such as electron wavefunction overlap and band alignment. The recent emergence of magnetic two-dimensional materials opens new possibilities for exploring proximity effects in van der Waals heterostructures13–16. In particular, atomically thin CrI3 exhibits layered antiferromagnetism, in which adjacent ferromagnetic monolayers are antiferromagnetically coupled3. Here we report a layer-resolved magnetic proximity effect in heterostructures formed by monolayer WSe2 and bi/trilayer CrI3. By controlling the individual layer magnetization in CrI3 with a magnetic field, we show that the spin-dependent charge transfer between WSe2 and CrI3 is dominated by positively charged trion emission17, consistent with type-II band alignment. The WSe2/CrI3 heterostructures were fabricated by mechanical transfer of individual exfoliated WSe2 and CrI3 flakes in a glove box (Methods). A device schematic is shown in Fig. 1a, where WSe2 is on top of CrI3. The excitation laser was fixed at 1.96 eV and the optical axis and applied magnetic field are perpendicular to the sample plane. For measurement of monolayer WSe2 photoluminescence, we performed co-circular polarized excitation and detection (either σ+ / σ− or σ+/σ−) to read out the valley exciton information.

We first present the results from a monolayer WSe2/trilayer CrI3 heterostructure. Figure 1c shows circular polarization-resolved photoluminescence spectra at 15 K and zero magnetic field, which is dominated by positively charged trion emission17, consistent with type-II band alignment. The σ+/σ− photoluminescence (red curve) is stronger than the σ− /σ− (blue curve); this spontaneous circularly polarized photoluminescence demonstrates the breaking of valley degeneracy and thus time reversal symmetry of monolayer WSe2 by proximity to the magnetic trilayer CrI3. As discussed in ref. 17, when the photoexcited electron spin in WSe2 has the same orientation...
Fig. 1 | Proximity control of valley dynamics in monolayer WSe2 interfacing with trilayer CrI3. a, Schematic of monolayer WSe2 and trilayer CrI3 heterostructure. b, Schematic depicting spin-dependent charge transfer. Assuming spin-down magnetization CrI3, the optically excited spin-down electrons in the –K valley will transfer to the CrI3 spin-polarized 3d e_g band, while charge transfer of the spin-up electron in the +K valley is suppressed. c, Polarization-resolved photoluminescence of a WSe2/trilayer CrI3 heterostructure at 15 K and zero magnetic field, showing spontaneously σ+ polarized photoluminescence. d–f, Degree of circular polarization (d), valley Zeeman splitting in photoluminescence (e) and RMCD (f) as a function of magnetic field. Orange and green curves represent magnetic field sweeping up (increase) and down (decrease), respectively.

as the CrI3 magnetization, charge transfer is allowed (Fig. 1b). Otherwise, it is suppressed. This spin-dependent charge transfer from WSe2 to CrI3 gives rise to strong circularly polarized photoluminescence (Fig. 1c).

To investigate the relationship between the proximity effect and magnetic states, we measured polarization-resolved photoluminescence and reflective magneto-circular dichroism (RMCD) as a function of applied magnetic field at 15 K. In labelling the magnetic states of CrI3, below, we count the CrI3 layers from top to bottom, where the top layer interfaces with WSe2. We quantify the photoluminescence polarization as $\rho = (I_\sigma - I_{-\sigma})/(I_\sigma + I_{-\sigma})$, where $I_\sigma$ ($I_{-\sigma}$) represents photoluminescence intensity with co-$\sigma^+$ (co-$\sigma^-$) excitation and detection. In addition to spin-dependent charge transfer, the magnetic exchange field introduces an excitonic valley Zeeman splitting, which is defined as $\Delta = E_{\sigma^+} - E_{\sigma^-}$. Here, $E_{\sigma^+}$ ($E_{\sigma^-}$) is the peak energy of $\sigma^+/\sigma^-\sigma$ photoluminescence from +K (–K) valley trions (Supplementary Text 1). Figure 1d–f plots $\rho$, $\Delta$ and RMCD signal as a function of magnetic field, respectively. Consistent with previous reports, the RMCD signal in Fig. 1f shows three transitions in a given field sweep (at about ±1.6 T and ±0.2 T), with each corresponding to a flip in layer magnetization. The magnetic states, which consist of two fully spin-polarized states ↑↑↑ and ↓↓↓, and two layered AFM states ↑↑↓ and ↓↓↑, are indicated in Fig. 1f.

As shown in Fig. 1d,e, the evolution of magnetic states as a function of magnetic field is also manifested in both $\rho$–H and $\Delta$–H traces. We first focus on the $\rho$–H trace and sweep the magnetic field up from large negative field where the CrI3 trilayer is fully polarized (↓↓↓). Owing to Hund’s coupling in the Cr ions, photoexcited electrons with spin down in WSe2 transfer more efficiently to CrI3, resulting in stronger $\sigma^+$ polarized photoluminescence. As the magnetic field increases beyond −1.6 T, CrI3 transitions from ↓↓↓ into ↑↓↓ with the middle layer flipping its magnetization. Correspondingly, $\rho$ decreases slightly, by about 16%. Further increasing the magnetic field to be above 0.2 T causes CrI3 to transition into ↑↑↑ with the top layer flipping its magnetization. As a result, $\rho$ sharply changes from positive to negative since electrons with spin up are now favoured to transfer from WSe2 to CrI3. When the magnetic field is larger than 1.6 T, CrI3 becomes fully spin polarized (↑↑↑) and $\rho$ reaches maximum negative value. The $\rho$–H trace implies that the spin-dependent charge transfer is dominated by the interfacial top layer, whereas the middle layer, 0.7 nm away below the interface, has a measurable but much weaker effect.

In contrast to $\rho$, the proximity exchange field, and thus the induced valley Zeeman splitting $\Delta$ has a distinct dependence on the magnetic states. As shown in Fig. 1c, when CrI3 is the AFM states, $\Delta$ is much larger than it is for the fully spin-polarized states. This is quite surprising since the proximity exchange field is from a short-range interaction and, thus, it is expected to be dominated by the magnetization in the top layer. The pronounced difference in the proximity exchange field between the fully spin polarized and AFM states (for example, ↑↑↑ and ↓↓↓) is unexpected.

This observation is further corroborated by measurements on a monolayer WSe2/bilayer CrI3 device (BD1) at 1.6 K. Figure 2a shows a schematic of the bilayer heterostructure. The RMCD signal in Fig. 2b is typical of bilayer CrI3, showing two AFM states (↑↑↑ and ↓↓↓) and two fully spin-polarized ferromagnetic (FM) states (↑↑↓ and ↓↓↑). Figure 2c shows the photoluminescence intensity plot of $\rho$–(σ−−σ−) (left) and co-$\sigma^+$ (right) excitation and detection as a function of magnetic field and photon energy. Sharp changes are identified near the transition of the CrI3 magnetic states. The extracted $\rho$–H curve in Fig. 2d shows that $\rho$ reaches maximum when CrI3 is in the fully spin-polarized states and has a slight decrease in the CrI3 AFM states. In contrast, in Fig. 2e, AFM states produce larger valley Zeeman splitting than the FM states.

The distinct behaviour between $\rho$ and $\Delta$ can be explained as follows. The photoluminescence polarization $\rho$ is determined by the real hopping of electrons from WSe2 to CrI3, accompanied by...
Fig. 2 | Proximity effect in a monolayer WSe₂/bilayer CrI₃ heterostructure. a, Schematic of a monolayer WSe₂ and bilayer CrI₃ heterostructure. The layered AFM domains that are indistinguishable by RMCD can be resolved by circular polarization-resolved photoluminescence from WSe₂. b, RMCD as a function of magnetic field, showing typical features of a layered AFM bilayer CrI₃. We note that the tiny residual RMCD signals of the AFM states cannot be used to distinguish the two AFM states (see Supplementary Fig. 3). c, Photoluminescence intensity plot of co-σ⁺ (left) and co-σ⁻ (right) polarized excitation and detection as a function of magnetic field and photoenergy. d,e, Degree of circular polarization (d) and valley Zeeman splitting (e) as a function of magnetic field, extracted from data in c. The data were acquired from device BD1.

Fig. 3 | Imaging layered AFM domains in bilayer CrI₃ by monolayer WSe₂. a, Spatially resolved RMCD (bottom) and spontaneous circular polarization ρ of WSe₂ photoluminescence (top) as the device BD1 was ZFC down to 1.6 K. Scale bar, 2 μm. b, Spatial map of ρ at zero magnetic field as CrI₃ is initialized in the ↓↓ state by applying negative magnetic field. The labels I and II denote two layered AFM domains. c, The same as b but with CrI₃ initialized at the ↑↑ state by applying large positive magnetic field. d,e, ρ as a function of magnetic field at selected spots in domains I (d) and II (e). Insets depict the magnetic states.
energy relaxation. In contrast, the proximity exchange field is primarily from a second-order virtual hopping process that shifts the WSe$_2$ band edge of certain spin species by the conduction or valence band shift $\Delta_{\text{v}}/\Delta_c \sim \frac{t^2}{|E|}$, where $t$ is the hopping matrix element between WSe$_2$ and CrI$_3$, and $E$ is their band offset. In the AFM configuration (for example, ↑↑), the antiparallel spin alignment of adjacent CrI$_3$ monolayers suppresses the interlayer hopping of charge carriers, which is otherwise significant in the fully spin aligned configuration (for example, ↑↑). This magnetic-configuration-dependent interlayer hopping between CrI$_3$ layers leads to significantly different band energy and the observed change in $\Delta$ can be reproduced with reasonable choices of $t$ and band offset $\Delta E$ (see Supplementary Text 2), while the precise determination of these parameters requires further experimental (for example, angle-resolved photoemission spectroscopy) and computational studies.

The sensitive dependence of the proximity effect on the spin structure of CrI$_3$, shown above allows us to use monolayer WSe$_2$ as a magnetic sensor to probe the domain structures and dynamics in layered AFM bilayer CrI$_3$. As demonstrated in Fig. 2a, since bilayer CrI$_3$ has vanishing magnetization in the AFM configuration, RMCD alone cannot probe the domain effects. However, the photoluminescence polarization, $\rho$, is dominated by the interfacial layer, thus providing an excellent probe of magnetization in the top CrI$_3$ layer. Combined with RMCD, which probes the total magnetization of the bilayer, we can construct the layered AFM domains.

Figure 3a shows the intensity map of $\rho$ (top) and RMCD signal (bottom) of device BD1. The data was acquired after the sample was zero-field-cooled (ZFC) down to 1.6 K. The map of $\rho$ is composed of positive and negative polarization patches, which corresponds to the up and down magnetization domains of the top layer in the CrI$_3$ bilayer. On the other hand, the RMCD map (bottom panel) has nearly zero intensity across the whole heterostructure, showing that bilayer CrI$_3$ is in an AFM ground state. The comparison of both maps reveals the spontaneous formation of ↑↑ and ↓↓ layered AFM domains.

The spontaneously formed layered AFM domain walls can be reconfigured by applying an external magnetic field. For instance, after initializing the bilayer to the ↓↓ state by a large negative magnetic field, we sweep the magnetic field back to zero. The resulting spatial map of $\rho$ in Fig. 3b shows two dominant layered AFM domains, labelled I and II. We can also initialize the bilayer in the ↑↑ state and then sweep the magnetic field back to zero. The corresponding spatial map of $\rho$, shown in Fig. 3c, is a time reversal of Fig. 3b. Figure 3d,e shows $\rho-H$ at two selected spatial points in domains I and II, respectively. When the magnetic field sweeps up, at around $-0.5$ T, the magnetic states switch from FM to AFM; $\rho$ drops slightly in domain I (Fig. 3d), whereas it changes drastically and reverses sign in domain II (Fig. 3e). These data demonstrate that the top layer in the CrI$_3$ bilayer flips magnetization first in domain II, whereas the bottom layer flips first in domain I (see Supplementary Fig. 3). Comparing Fig. 3b,c with Fig. 3a, we can see that among the spontaneously formed layered AFM domains in Fig. 3a, the domain wall that separates domain I and domain II is pinned, whereas the multiple domain walls in the ZFC case located inside domain I are moveable and reconfigured after magnetization initialization. This pinned domain II is probably due to strain introduced by the heterostructure fabrication.

We found that the domain structures vary between devices, probably caused by the uncontrolled heterostructure fabrication process. Figure 4 shows another example (device BD2) measured at 6.6 K. The ZFC domain structure is mainly dominated by two layered AFM domains (Fig. 4a). After the bilayer CrI$_3$ has been initialized by the magnetic field, the layered AFM domains at zero field vanish and only a single domain exists (Fig. 4b). However, at finite magnetic fields, we observed a layered AFM/FM domain wall. For instance, as the magnetic field increases from zero, a ↑↑ domain forms first at the bottom left corner of the heterostructure at a magnetic field of 0.25 T, whereas the rest of the sample is still in the ↓↓ state. Distinct $\rho-H$ traces from these two domains are shown in Supplementary Fig. 4. Compared to BD1, this device has less
complicated domain structures at zero magnetic field, which may indicate a better transfer with a more homogeneous strain distribution. We have also observed complicated, layered AFM/FM domain patterns in a less homogeneous sample compared to device BD2 (see Supplementary Figs. 5–7), where the inhomogeneity is probably from strain introduced in the heterostructure transfer process (see Supplementary Fig. 8).

In summary, our work provides insights into the magnetic proximity effects of a vdW magnetic heterostructure by utilizing the multiple magnetic configurations accessible in layered AFM CrI₃. This understanding will be important for developing magnetic vdW devices. In addition, we establish the ability to image layered AFM domains within a vdW magnet using the spin-valley properties of a monolayer semiconductor, which would be challenging with conventional magnetometry techniques. Furthermore, our observation of possible strain-induced domain behaviour highlights the effect of strain in determining magnetic states in vdW magnets. Thus, we suggest that strain engineering is a promising direction for future studies to enhance the versatility and controllability of vdW magnets in spin and valleytronics applications.

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Methods

Device fabrication. Monolayer WSe₂ and hexagonal boron nitride (hBN) flakes were exfoliated under ambient conditions and then transported into the glove box. CrI₃ flakes were exfoliated onto a 90-nm silicon oxide/silicon wafer inside the glove box with <0.5 ppm O₂ and <0.5 ppm H₂O environment. We identified bilayer CrI₃ by optical contrast, which was further confirmed by RMCD in the experiment. Immediately after finding the bilayer, we assembled the heterostructure by polycarbonate-based dry transfer. After hBN encapsulation, the heterostructures were stable in an ambient environment, which allowed us to remove them from the glove box and load them into an optical cryostat for measurements.

Optical measurements. Optical measurements were performed using the setup detailed in ref. 17. We used a HeNe laser (1.96 eV) for both polarization-resolved photoluminescence and RMCD measurements. In both cases, the laser was normally incident on the sample with a beam spot size of about 1 µm diameter. For photoluminescence measurements, we used 3 µW for spatially resolved maps and 10 µW for magnetic field sweeps. For RMCD measurements, we used the same excitation power as the photoluminescence measurements for spatially resolved maps and magnetic field sweeps. The experimental setup is detailed in ref. 20.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
X.X., W.Y., and D.X. conceived the project. D.Z. fabricated the sample. D.Z., K.L.S., and X.L. performed the experiment assisted by N.P. W. X.X. and K.-M.C.F. supervised the experiment. M.A.M. synthesized and characterized the bulk CrI₃ crystal. T.T. and K.W. synthesized the bulk hBN crystal. D.Z., X.X., W.Y., and D.X. analysed the data. X.X., D.Z., K.L.S., W.Y., and D.X. wrote the paper with input from all authors. All authors discussed the results.

Competing interests
The authors declare no competing interests.

Additional information
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