Interplay between spin proximity effect and charge-dependent exciton dynamics in MoSe$_2$/CrBr$_3$ van der Waals heterostructures

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Semiconducting ferromagnet-nonmagnet interfaces in van der Waals heterostructures present a unique opportunity to investigate magnetic proximity interactions dependent upon a multitude of phenomena including valley and layer pseudospins, moiré periodicity, or exceptionally strong Coulomb binding. Here, we report a charge-state dependency of the magnetic proximity effects between MoSe$_2$ and CrBr$_3$ in photoluminescence, whereby the valley polarization of the MoSe$_2$ trion state conforms closely to the local CrBr$_3$ magnetization, while the neutral exciton state remains insensitive to the ferromagnet. We attribute this to spin-dependent interlayer charge transfer occurring on timescales between the exciton and trion radiative lifetimes. Going further, we uncover by both the magneto-optical Kerr effect and photoluminescence a domain-like spatial topography of contrasting valley polarization, which we infer to be labyrinthine or otherwise highly intricate, with features smaller than 400 nm corresponding to our optical resolution. Our findings offer a unique insight into the interplay between short-lived valley excitons and spin-dependent interlayer tunneling, while also highlighting MoSe$_2$ as a promising candidate to optically interface with exotic spin textures in van der Waals structures.
Few of the materials which have underpinned solid-state physics research over the past century now lack a 2-dimensional crystalline analog. This is keenly exemplified by recent discoveries of long-range magnetic order persisting into the monolayer limit in 2-dimensional van der Waals materials. However, the true potential of layered crystals lies not simply in having access to a selection of atomically thin proxies for conventional materials, but rather the ability to easily stack and combine these different materials into arbitrarily designed van der Waals heterostructures. Not only are such composites free of conventional materials, but rather the ability to easily stack and combine these different materials into arbitrarily designed van der Waals heterostructures.

In this context, the discovery of 2-dimensional magnets in particular realizes a step-change for the nascent field of wholly van der Waals based spintronics. One such material currently experiencing a resurgence of interest is chromium tri-bromide (CrBr3), a layered ferromagnetic semiconductor with Curie temperature 37 K and magnetization 3.85 μB per Cr atom along the easy c-axis. Recent work suggests that, in stark contrast to few-layer CrI3 and CrCl3 flakes which both exhibit antiferromagnetic interlayer ordering, the interlayer exchange in exfoliated CrBr3 is ferromagnetic, although it can depend on stacking order.

The incorporation of this emerging family of magnetic materials with optically active transition metal dichalcogenides (TMDs) is expected to combine the advantageous chiral optical selection rules and spin-valley locking of TMDs with the highly correlated and field-responsive long-range ordering inherent to magnets. Proximity effects between monolayer TMDs and van der Waals ferromagnets have so far manifested as enhanced valley Zeeman splitting and/or modifications to the photo-luminescence (PL) intensity. Where changes in the circular polarization degree of PL are reported, significantly broadened linewidths preclude the extraction of useful spectral information, and individual excitonic states cannot be resolved.

In this work, we study a van der Waals interface formed between the TMD molybdenum diselenide (MoSe2) and ferromagnetic CrBr3. While the interlayer band alignment is nominally type-II, with the global conduction band minimum found in CrBr3, a strong spin polarization of the CrBr3 conduction bands gives rise to spin-dependent interlayer charge transfer rates for electrons tunneling from MoSe2 to CrBr3. This spin-dependent non-radiative decay channel causes a valley-dependent quenching of MoSe2 photoluminescence intensity, leading to a strongly enhanced degree of circular polarization (DOCP). Crucially, the DOCP is observed only in the MoSe2 trion state, rather than the neutral exciton, thereby providing insight into the interlayer tunneling timescales, which we infer to lie between the exciton and trion radiative lifetimes.

**Results**

**MoSe2/CrBr3 van der Waals heterostructures.** The sample consists of a monolayer of MoSe2 placed directly on top of ~7–8 nm thick multilayered CrBr3, with few-layer hBN encapsulating the structure on both sides, as shown in Fig. 1a. The hBN encapsulation is necessary here owing to the extreme environmental sensitivity of exfoliated CrBr3, a property shared also with CrI3, in which degradation occurs rapidly under exposure to air and moisture, in a reaction catalyzed by light. The residue-free transfer techniques

![Fig. 1 MoSe2/CrBr3 van der Waals heterostructures.](image-url)

**Fig. 1 MoSe2/CrBr3 van der Waals heterostructures.** a Microscope image of the sample in this work showing multi-layered CrBr3, monolayer MoSe2, and hBN encapsulation layers. b Photoluminescence spectrum from the sample under continuous-wave laser excitation at 1.946 eV and a sample temperature of 4.2 K. Neutral exciton (X) and trion (T) peaks are visible. c, d Schematics of a MoSe2/CrBr3 heterobilayer structure used in the density functional theory calculations, viewed from the side (c) and top (d), where the supercell is highlighted. Here, the experimental lattice constant of monolayer MoSe2 is applied to both layers, in order to simplify the calculations, along with setting the relative crystallographic twist angle to zero between the layers (see Supplementary Note 1). Crystal images were produced using VESTA software. e The DFT calculated electronic band structure of the MoSe2/CrBr3 heterobilayer, projected on the host material. The global valence band maximum is localized in MoSe2 at E = 0. The green band color indicates hybridization between the two materials. The e_g orbitals have spin polarization opposite to the t_{2g} orbitals.
used during fabrication (see Methods) ensure full contact between the MoSe₂ and CrBr₃, such that trapped contaminants do not inhibit the interlayer charge transfer and proximity induced magnetic exchange effects. Photoluminescence (PL) from the sample at 4.2 K under non-resonant optical excitation at 1.946 eV displays a spectrum quite characteristic of MoSe₂, with a high energy peak ascribed to the neutral exciton (X) and a lower energy peak attributed to the charged exciton, or trion (T) (Fig. 1b)³⁵,³⁶. However, the emission intensity from the sample is far lower than typical for exfoliated MoSe₂, indicating a quenching of PL due to loss of photocarriers from MoSe₂ into CrBr₃, reducing the quantum yield.

Density functional theory (DFT) calculations of the electronic band structure of a MoSe₂/CrBr₃ heterobilayer (Figs. 1c, d) indicate a type-II interlayer band alignment, with the global conduction band (CB) minimum located in the CrBr₃ layer, as shown in Fig. 1e. As the material bandgaps depend sensitively on ligand electronegativity, the exact interlayer band alignment at the interface depends heavily on the elemental compositions of each layer²⁷. (For details of the DFT calculations see Supplementary Note 1). Photogenerated electrons are predicted to scatter from the MoSe₂ CB into the CrBr₃ CB, introducing an additional non-radiative decay channel, corroborating with the observed suppressed luminescence intensity. Such interlayer charge transfer may be aided by electronic interlayer hybridization between the two materials, seen in Fig. 1e as green-shaded regions. Any instances of hybridization would be expected to lead to efficient interlayer charge transfer, via elastic scattering events. Additionally, this heterostructure band alignment suggests that a static electron doping cannot exist in the MoSe₂ layer, while holes will accumulate in the MoSe₂ valence band (VB) as electrons tunnel out of the CB non-radiatively. Therefore, we attribute the observed trion luminescence to positively charged excitons, whereby neutral excitons bind to resident holes in the MoSe₂ VB³⁰,³⁵.

A crucial feature of our experiment is that our laser, at 1.946 eV, lies directly in an absorption minimum of CrBr₃³⁸–⁴⁰. In this way, we ensure that photoexcitation occurs only in MoSe₂, and so no electron-hole pairs are created in CrBr₃. Therefore, with the exception of possible electrostatic discharge when the interface is first formed during sample fabrication, we can confidently neglect appreciable hole tunneling from CrBr₃ to MoSe₂. As confirmation that our laser is not being absorbed, we search for direct CrBr₃ luminescence, reported at 1.35 eV under 1.77 eV illumination²³. Despite rigorous searching, we observe nothing but MoSe₂ PL between the laser energy and the limit of our detector sensitivity, ~1.1 eV, consistent with CrBr₃ being transparent to our laser.

The calculated electronic band structure in Fig. 1e also reveals a strong exchange splitting of the CrBr₃ CB, which is comprised of Cr³⁺d-orbitals. Bands arising from the majority-spin εₓ orbitals can be seen in red between 0.5 and 1 eV, while the minority-spin τ₂g orbitals form bands at 1.5 eV and above¹¹,⁴². Importantly, below the CrBr₃ Curie temperature ~ 37 K, these two sets of bands are oppositely spin-polarized out of the sample plane. This is intrinsically tied to the local CrBr₃ magnetization, such that when the magnetization is flipped between pointing up or down out of the plane, the spin polarization of these two sets of bands reverses. Since the εₓ orbitals constitute the majority-spin, they are spin↑ (spin↓) when the local CrBr₃ magnetization points upwards (downwards) out of the sample plane, while the τ₂g orbitals are spin↓ (spin↑).

Although our sample is not a heterobilayer, but rather multi-layered CrBr₃, we expect any magnetic proximity effects to arise primarily from the topmost CrBr₃ layer, owing to the very short range of exchange interactions and interlayer orbital wavefunction overlap²²,⁴³. We confirm this by calculating and comparing the band structures of MoSe₂/1L CrBr₃ and MoSe₂/2L CrBr₃, and observe only negligible differences between the two (see Supplementary Note 2).

Polarization resolved magneto-photoluminescence. In order to gain insight into the valley pseudospin dynamics in our sample, we detect PL in σ⁺ and σ⁻ circular polarizations while sweeping an external magnetic field (B) perpendicular to the sample plane, within the range B = ±200 mT, in both forward (negative to positive) and backward (positive to negative) sweep directions, at 4.2 K. A B-field orientation upwards (downwards) out of the plane is positive (negative). Fig. 2a shows the σ⁺ polarized PL as a function of emitted photon energy and B-field, in the forward sweep direction. As can be seen, the trion intensity sharply increases at B = −20 mT, followed by a steady further increase, until the intensity reaches a plateau at B ~ 50 mT. This striking response must be attributed to the influence of CrBr₃, as the PL intensity of an isolated MoSe₂ monolayer would change only negligibly under the application of such weak external B-fields as used here. In stark contrast, the excition emission, notably distinct from the trion, exhibits no observable change in intensity.

Bright neutral excitons are comprised of an electron-hole pair located in either the K or K’ valley, corresponding to the σ⁺ or σ⁻ polarization state of the emitted photon (Fig. 2b)²⁹. To form a positively charged trion, the exciton binds to an additional hole in the opposite valley (Fig. 2b)³⁵,⁴⁶. This intervalley ground state is highly favored over the intravalley trion configuration, for which the large ~200 meV spin-orbit coupling strength in the VB is prohibitive. The electron spin is tied to the emission helicity owing to optical selection rules and spin-valley locking²⁹,⁴⁶.

To elucidate the trion magneto-optical response, we plot the integrated trion intensity in both circular polarizations, in both forwards and backwards B-field sweep directions, as shown in Fig. 2c. As can be seen, the trion intensities in opposite polarizations behave exactly symmetrically, such that when the intensity of one polarization decreases the other increases by the same amount. In both sweep directions, the intensities invert as B passes through zero, indicating a clear reversal of trion valley populations when very small B-fields are applied. A specific response to the sweep direction which is symmetric about zero-field, as seen here, is a hallmark of ferromagnetism, confirming the influence of CrBr₃ on the MoSe₂ trion state valley polarization.

A powerful tool to investigate the valley pseudospin dynamics in the sample is the DOCP, (Iₓ+−Iₓ−)/(Iₓ+ + Iₓ−), of the emitted luminescence. Fig. 2d presents the DOCP as a function of photon energy and applied B-field, in the forward sweep direction. Here, a very prominent trion switching can be seen between robust positive and negative DOCP, while the exciton state remains apparently insensitive to any interactions with CrBr₃. Plotting the DOCP using integrated intensities, in both sweep directions, as shown in Fig. 2e, brings the sweep direction-dependent response into sharp focus. While the exciton remains at zero, the trion state follows a sweep-dependent path when switching between the two valley polarized extremes, revealing the existence of two hysteretic lobes in the DOCP. We have fabricated and studied an additional 2 samples, both of which reproduce the trion DOCP sensitivity and exciton insensitivity observed in sample 1 (See Supplementary Note 3). Furthermore, by heating the sample under a fixed applied B-field, we observe the DOCP to tend to zero above the reported Curie temperature of CrBr₃ ~ 37 K (See Supplementary Note 4)²⁷.

Spin-dependent interlayer charge transfer. Ostensibly, an enhanced DOCP in MoSe₂ trion luminescence indicates a finite
valley polarization in the resident carrier population. However, in this case, a hole valley polarization may be ruled out as the origin of the observed trion DOCP for three reasons. Firstly, any imbalance between the itinerant carrier populations of the two valleys leads not only to a change in trion intensity, but also to an opposite and proportional change in exciton intensity, owing to the intervalley nature of the trion ground state. We observe no corresponding change in exciton intensity in Fig. 2a, and no mirroring of the trion DOCP by the exciton DOCP in Figs. 2d and e. Secondly, the observed trion DOCP cannot be due to a suppression of intervalley relaxation, as the sign of the DOCP is independent of the polarization state of the laser, and so the system retains no memory of optical valley initialization (see Supplementary Note 5). Thirdly, our DFT calculations predict a negligible proximity induced spin splitting in the MoSe2 VB maxima, thereby precluding the generation of a static valley polarization in the itinerant hole population in thermal equilibrium. The band dependence of the proximity induced spin splitting is ultimately related to their different orbital content, with the VB orbitals constituting the MoSe2 CB edges do protrude more out of the molybdenum plane, and so experience a modest spin splitting due to proximity, which we measure to be <0.5 meV (Supplementary Notes 1 and 6). Regardless, this splitting is in the CB and so cannot generate a static hole valley polarization in the VB.

Therefore, rather than a static hole valley polarization, we attribute the observed DOCP to spin-dependent interlayer electron transfer, which translates to valley-dependent charge leakage from MoSe2 owing to the spin-valley locking effect. Similar results have previously been observed in conventional ferromagnet-quantum well systems. The particular interlayer band alignment in this structure results in the MoSe2 CB being resonant only with the minority-spin ($\sigma^-$) bands of CrBr3, while the majority-spin ($\sigma^+$) bands are non-resonant by several hundred meV (Fig. 1e). Therefore, we expect that photogenerated electrons in the MoSe2 CB will be able to tunnel into the CrBr3 CB more efficiently if they are spin aligned with the CrBr3 minority-spin states. In order to tunnel into the majority-spin bands, multiple phonon scattering or high energy Auger-like interactions would be required, resulting in poor tunneling efficiency (Fig. 3a). We also note the aforementioned lack of absorption of our laser by CrBr3, which ensures that dynamic hole transfer (spin-dependent or otherwise) from CrBr3 into MoSe2 can safely be neglected.

Consequently, we can be confident that the observed trion DOCP arises purely from electron tunneling from MoSe2 into CrBr3, which introduces an additional non-radiative decay for K or K' valley trion states, depending on the CrBr3 magnetization.

We note that our PL signal is comparably quenched in both $\sigma^+$ and $\sigma^-$ polarizations, yet shows a 10% DOCP in the trion state. We attribute this to a complex interplay between exciton valley dynamics and spin-dependent interlayer charge transfer in our sample. In MoSe2, the exciton dispersion experiences an energy...
splitting between excitons with dipole moment parallel (longitudinal, L) or perpendicular (transverse, T) to their in-plane wavevector, \( \mathbf{k} \), arising from the long range electron-hole exchange interaction\(^{50,51}\). This L-T splitting is linearly proportional to \( \mathbf{k} \) outside the light cone, and manifests as an effective magnetic field acting on the exciton valley pseudospin, creating precession and associated valley depolarization, aided by disorder scattering\(^{50-52}\). Consequently, valley depolarization is extremely efficient (\(<0.1\) ps\(^{53}\)) for high-\( \mathbf{k} \) excitons, and suppressed for low-\( \mathbf{k} \) excitons (Fig. 3b). As such, any valley polarization from interlayer tunneling at higher energies (closer to the laser at 1.946 eV) is quickly erased, and the tunneling serves only to uniformly quench both the \( \sigma^+ \) and \( \sigma^- \) PL spectra. We expect the tunneling to be very efficient at these higher energies owing to resonant interlayer band alignment and regions of hybridization evident in Fig. 1e between the MoSe\(_2\) CB and CrBr\(_3\) \( t_{2g} \) states. This efficient hot electron tunneling will indeed be highly spin polarized, but the comparably fast valley depolarization in MoSe\(_2\) ensures that no signatures persist in the observed DOCP.

We therefore believe that the measured DOCP is sensitive only to spin/valley dynamics in the energy range corresponding to vanishing exciton center-of-mass momentum, close to or inside the light cone. At these low wavevectors, the exchange induced valley depolarization is weak, allowing spin-dependent tunneling to influence the DOCP in luminescence. The fact that DOCP is observed only in the trion state implies that the additional non-radiative decay arising from charge transfer in this low energy range must be slower than the exciton radiative lifetime (sub-ps\(^{54}\)), but faster than the lifetime of the trion state, which is an order of magnitude longer (\(>10\) ps\(^{55}\)). Our conclusion is supported by analysis of the PL linewidths, revealing a magnetization dependent change in the trion linewidth of \( \approx 1 \) meV, while the exciton linewidth remains constant (Fig. 3c). This allows us to estimate that the additional non-radiative decay experienced by the trion owing to spin-dependent charge transfer at these lower energies is \(\approx 0.7\) ps. The tunneling efficiency is generally influenced by various factors, including band hybridization, and energy or momentum offsets\(^{9,56-59}\). Our calculations (Fig. 1e) predict that at the bottom of the MoSe\(_2\) CB there is a low degree of hybridization with CrBr\(_3\) CB states, and the energy and momentum offsets for possible electron scattering are large. These factors can explain the relatively long charge transfer times deduced from the experiment. We note that the tunneling rates may vary over a large range, as was revealed in recent pump-probe experiments on twisted TMD heterobilayers, where sub-ps to 5 ps tunneling times were observed, drastically dependent on the relative crystallographic twist angle between the layers\(^{57}\).

In stark contrast to MoSe\(_2\), the valley pseudospin lifetime in WSe\(_2\) exceeds the PL lifetime\(^{60}\), and so the final PL DOCP will be influenced by the full extent of spin-dependent interlayer tunneling occurring between the laser energy and the PL energy. This explains why the reported DOCP in WSe\(_2\)/CrI\(_3\) structures is larger than our MoSe\(_2\) case, while also explaining why we observe no dependence on laser polarization in our sample (Supplementary Note 5), whereas results from WSe\(_2\)/CrI\(_3\) structures depend fundamentally on the laser polarization\(^{50}\).

**Domain-like valley polarization topography.** The intertwined relationship between trion PL and the local magnetization of CrBr\(_3\), as demonstrated in Fig. 2c, means that the DOCP serves as a proxy magnetization or M-H curve. Viewed in this way, the trion polarization degree bears all the hallmarks of the magnetization response of a thin ferromagnetic film with perpendicularly magnetocrystalline anisotropy, in which the magnetization of each domain must be aligned upwards or downwards out of the plane\(^7,25,61\). When \(|B| > B_{\text{sat}} = 50\) mT, plateaus are observed, corresponding to magnetic saturation parallel to the external field, whereby the CrBr\(_3\) is essentially in a single magnetic domain state. At field strengths lower than the saturation field, a complex response is observed featuring two marked hysteretic lobes, with a smooth linear gradient around \(B = 0\). Such a dependence is purely the result of magnetic domain dynamics, whereby the two discontinuities at

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**Fig. 3 Spin-dependent interlayer tunneling.** a Schematic of spin-dependent interlayer charge transfer over the MoSe\(_2\)/CrBr\(_3\) interface. The type-II band alignment precludes a static electron doping in MoSe\(_2\), and so we infer a resident hole population. In CrBr\(_3\), the CB is strongly split into oppositely spin-polarized bands. Only the minority-spin bands are resonant with the MoSe\(_2\) CB. Upon optical injection of electron-hole pairs, the electrons may tunnel from MoSe\(_2\) to CrBr\(_3\), with efficiency depending on their spin (green or purple indicate opposite spin). As CrBr\(_3\) is transparent at our laser energy, absorption is negligible, and so we expect no appreciable dynamic hole transfer from CrBr\(_3\) to MoSe\(_2\). b Diagram of exciton dispersion in MoSe\(_2\), with an energy splitting (the L-T splitting, see main text) proportional to in-plane wavevector \( \mathbf{k} \). The L-T splitting acts as an effective magnetic field inducing valley pseudospin relaxation in the presence of disorder scattering. Outside the light cone, efficient valley depolarization prevents spin-dependent tunneling from influencing the eventual DOCP. At low \( \mathbf{k} \), the spin-dependent tunneling is able to influence the DOCP observed in PL. At vanishing center of mass momentum, the exciton population either radiatively recombines (sub-ps) or else binds to a resident hole to form a long-lived trion valley state, which will be susceptible to spin-dependent tunneling. c Polarization resolved PL linewidths of the exciton (X) and trion (T). The trion linewidth shows opposing behavior in different polarizations, indicating that the lifetime is influenced by spin-dependent interlayer tunneling. The exciton has a constant linewidth, indicating insensitivity to CrBr\(_3\) magnetization.
\[ B = \pm 20 \text{ mT} \] appear as a result of spontaneous magnetic nucleation\textsuperscript{25,61}. This process occurs when a saturating \( B \)-field is gradually removed, until a balance is tipped in favor of the formation of antiparallel adjacent domains, representing a lower energy configuration. For the metastable saturation state to break down, a potential barrier associated with domain wall formation must be overcome\textsuperscript{51}.

At very low fields, \( |B| < 20 \text{ mT} \), the average magnetization responds linearly to \( B \) owing to unopposed lateral domain wall motion through the flake, allowing domains to grow and shrink as appropriate. As the CrBr\(_3\) flake is a single crystal, domain wall motion ought to be generally unobstructed, in contrast to polycrystalline thin-film ferromagnets, in which grain boundaries may impede domain growth\textsuperscript{62}. Introducing certain defects and disorder to the flake may also lead to domain wall pinning which opens up a hysteresis loop at zero field, consistent with the more typical remanence signatures of conventional ferromagnets\textsuperscript{4,43}.

As such, the absence of coercivity in this sample indicates both a weak anisotropy\textsuperscript{24}, and a low density of defects of the type which may impede lateral domain wall motion\textsuperscript{51,63}. However, we note that there may be a high density of other defects which have a weaker influence on domain dynamics, consistent with the unstable nature of CrBr\(_3\) (see Supplementary Note 8).

The crucial consequence of these CrBr\(_3\) domain dynamics is that the spin-dependent interlayer charge transfer in the heterostructure adopts a spatial topography and magnetic response describable by the physics of ferromagnetic domains. As shown in Fig. 4a, when \( B > B_{\text{sat}} (B < -B_{\text{sat}}) \), the charge transfer is preferentially spin-\( \uparrow \) (spin-\( \downarrow \)) over the entire interface. However, when \( |B| < B_{\text{sat}} \) the interlayer charge transfer rates adopt a highly contrasting spatial arrangement over the sample, which in turn creates domain-like regions of opposite valley polarization co-existing in the MoSe\(_2\) trion population. Cumulatively, a reversal of the external \( B \)-field gives efficient selectivity between opposite preferential tunneling rates for electrons of spin-\( \uparrow \) or spin-\( \downarrow \), while control of the field strength close to zero allows fine-tuning of their relative prevalence.

We note that in our PL experiments, we measure an average of domain activity within the area of our laser spot, \( \sim 5 \mu m^2 \). In order to gain insight into the characteristic length scales of the trion valley polarization domains in our sample, we measure the local magnetization via the polar magneto-optical Kerr effect (MOKE) in an optical microscope utilizing broadband illumination and wide-field high spatial resolution detection (Fig. 4b). We expect that the polar Kerr signal arises mainly from the CrBr\(_3\) layers of the sample, given the maximum of the illumination energy at 2.7 eV closely matches the CrBr\(_3\) main absorption resonance at 2.5 eV\textsuperscript{37}. Therefore, the close agreement between the PL from MoSe\(_2\) and the Kerr signal indicates a robust proximity effect and strong layer interaction\textsuperscript{64}. Despite our MOKE measurement area being \( \sim 0.5 \mu m^2 \), an order of magnitude smaller than in the PL experiment, there is close agreement between the two magneto-optical techniques, indicating that the domains are significantly smaller than the length scales of our optical probes. Indeed, no domain activity could be resolved in the Kerr microscope at all, confirming a domain size smaller than the optical resolution of the system, \( \sim 400 \text{ nm} \) (See Supplementary Note 8). High spatial resolution techniques such as scanning probe magnetometry would be required to resolve the domain structure in our sample\textsuperscript{5,65}.

Our findings are in good agreement with previous work on CrBr\(_3\) flakes in which electron microscopy reveals stripe domains with widths between 20 and 200 nm\textsuperscript{66}. In thin-film ferromagnets such as our CrBr\(_3\) flake, the domain size is governed by a complex interplay between magneto-crystalline and shape anisotropies, domain wall width, in-plane remanence, exchange energy, and magnetostatic interaction energy between the top and bottom film surfaces\textsuperscript{67}. The domain dynamics will therefore depend sensitively on the specific balance of these parameters, leading to significant variation. Indeed, complex and diverse domain patterns have been observed in CrBr\(_3\) including stripe, honeycomb, bubble, and cone domain structures\textsuperscript{68}. Weak in-plane external \( B \)-field orientation, disorder, temperature, or unpredictable local fluctuations, can all influence the domain patterns formed during each \( B \)-field cycle, with no correlation expected between patterns present before and after each instance of saturation, unless external input is used to provide control\textsuperscript{68}. We note that the trion Bohr radius in MoSe\(_2\) (\( \sim 1 \text{ nm} \)), is 1–2 orders of magnitude smaller than the domain sizes inferred by our observations. This suggests that control of domain formation dynamics in CrBr\(_3\), by the techniques mentioned above, would generate desired spatial patterns of contrasting electronic and trionic spin-valley polarization in MoSe\(_2\), be they stripe, honeycomb, bubble, and so on, with important consequences for opto-spintronic device design at the nanoscale.

**Discussion**

To conclude, we observe spectrally dependent magnetic proximity effects in photoluminescence from monolayer MoSe\(_2\) in contact with few-layer CrBr\(_3\). The local out of plane...
magnetization in CrBr₃ is imprinted in the MoSe₂ trion state valley polarization, while the neutral excitation state bears no hallmarks of proximity interactions. We attribute the observed magneto-optical response to a spin-dependent interlayer charge transfer process, whereby electrons tunnel from the CB of MoSe₂ into the CB of CrBr₃ with differing rates depending on their real spin. This leaves the optically pumped exciton population in MoSe₂ subject to competing mechanisms of spin-dependent tunneling and valley pseudospin depolarization, ultimately leading to the observed charge-state dependency of the proximity effects in photoluminescence. Furthermore, we infer that in the absence of an applied B-field, the sample displays simultaneous manifestation of positive and negative valley polarization in the trion population, with an intricate spatial topography conforming to the magnetic domains of CrBr₃.

Our results demonstrate a highly localized (<400 nm) technique to engineer the interlayer tunneling rates of electrons in van der Waals heterostructures. The wide-ranging implications of this technique, for example, incorporation of a layered ferromagnet beneath a TMD heterobilayer to enable control of the interlayer exciton lifetime, or local spin and charge densities, serving as a powerful complementary technique to the design of the crystallographic twist angle. Such enticing avenues of band structure engineering are yet to be explored. A further tantalizing possibility is the mimicry of unconventional spin textures by 2-dimensional semiconductors in proximity to magnetic materials. The local sensitivity of excitonic valley polarization may be extended to employ monolayer MoSe₂ as an atomically thin optical probe for such exotic phenomena as skyrmions or domain wall racetrack devices, thus realizing a wealth of far-reaching consequences along the boundary between exciton physics and van der Waals spintronics.

Methods

Low-temperature magneto-optical spectroscopy. Low-temperature magneto-photoluminescence spectroscopy was performed by mounting the sample in a liquid helium bath cryostat at 4.2 K with free-space optical access and a superconducting magnet coil. Non-resonant continuous-wave excitation at 1.946 eV in either ε₀ or ε₀’ polarized radiation, along with helicity selective circularly polarized PL collection, directed through a 0.75 m spectrometer and onto a nitrogen-cooled high sensitivity charge-coupled device. The helicity of the laser has no influence on the results measured, as discussed in Supplementary Note 5. To obtain linewidths and valley Zeeman splitting of exciton and trion peaks, Gaussian peak fitting was carried out on the PL spectra, as discussed in Supplementary Note 6.

Density functional theory calculations. See Supplementary Notes 1 and 2.

Low-temperature wide field Kerr microscopy. Spatially resolved polar Kerr hysteresis loops were acquired at low temperature using a wide field Kerr microscope equipped with a small helium gas flow cryostat designed for microscopy. A long working distance, high numerical aperture (NA 0.7) objective lens was used to achieve a spatial resolution of 400 nm. Spatial stability was achieved by mounting the cryostat on a piezoelectric stage for active drift correction. Hysteresis loops were acquired from user-defined microscale regions of interest on the sample. The polar Kerr effect allowed sensitivity to the out-of-plane component of the magnetization in response to a magnetic field as it was swept perpendicular to the sample plane. The background was due to the Faraday rotation in the objective lens and cryostat window when subject to a field applied parallel to the polar axis. Differential imaging allowed non-magnetic contrast such as sample topography to be subtracted leaving only the contrast due to the out-of-plane component of the sample magnetization.

Sample fabrication. A heterostructure comprising of MoSe₂/CrBr₃, encapsulated within thin hexagonal boron nitride (hBN) layers was assembled on a DMR substrate (top layer ~100 nm SiO₂) following standard dry transfer procedures using a poly (methyl methacrylate) (PMMA) membrane. MoSe₂ crystals were exfoliated on a heterostructure comprising of MoSe₂/CrBr₃, with differing rates depending on their real spin. This leaves the optically pumped exciton population in MoSe₂ subject to competing mechanisms of spin-dependent tunneling and valley pseudospin depolarization, ultimately leading to the observed charge-state dependency of the proximity effects in photoluminescence. Furthermore, we infer that in the absence of an applied B-field, the sample displays simultaneous manifestation of positive and negative valley polarization in the trion population, with an intricate spatial topography conforming to the magnetic domains of CrBr₃.

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Methods

Low-temperature magneto-optical spectroscopy. Low-temperature magneto-p...
of an electrically tunable MoSe₂/CrBr₃ heterostructure. Phys. Rev. Lett. 124, 197401 (2020).

25. Zhang, Z. et al. Direct photoluminescence probing of ferromagnetism in monolayer two-dimensional CrBr₃. Nano Lett. 19, 3138–3142 (2019).

26. Chen, W. et al. Direct observation of van der waals stacking–dependent interlayer magnetism. Science 366, 983–987 (2019).

27. Tsuibokawa, I. On the magnetic properties of a CrBr₃ single crystal. J. Phys. Soc. Jpn. 15, 1664–1668 (1960).

28. Klein, D. R. et al. Enhancement of interlayer exchange in an ultrathin two-dimensional magnet. Nat. Phys. 15, 1255–1260 (2019).

29. Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. Nat. Phys. 10, 343–350 (2014).

30. Zhong, D. et al. Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics. Sci. Adv. 3, e1603113 (2017).

31. Tong, Q., Chen, M. & Yao, W. Magnetic proximity effect in a van der Waals moiré superlattice. Phys. Rev. Appl. 12, 024031 (2019).

32. Seyler, K. L. et al. Valley manipulation by optically tuning the magnetic proximity effect in WSe₂/CrI₃ heterostructures. Nano Lett. 18, 3823–3828 (2018).

33. Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallogr. 44, 1272–1276 (2011).

34. Bermudez, V. M. & McClure, D. S. Spectroscopic studies of the two-dimensional magnetic insulators chromium trichloride and chromium tribromide-I. J. Phys. Chem. Solids 40, 129–147 (1979).

35. Dillon Jr, J., Kamimura, H. & Remeika, J. Magneto-optical response of chromium trihalide monolayers: chemical trends. J. Mater. Chem. C 8, 8856–8863 (2020).

36. Gudelli, V. K. & Guo, G.-Y. Magnetism and magneto-optical effects in bulk and few-layer CrI₃: a theoretical GGA+U study. J. Phys. Chem. B 112, 50332 (2008).

37. Zollner, K., Faria Junior, P. E. & Fabian, J. Proximity exchange effects in MoSe₂ and WSe₂ heterostructures with CrI₃ Twist angle, layer, and gate dependence. Phys. Rev. B 100, 085128 (2019).

38. Li, Y. et al. Valley splitting and polarization by the Zeeman effect in MoSe₂. Phys. Rev. Lett. 113, 266804 (2014).

39. Wang, G. et al. Magneto-optics in transition metal diselenide monolayers. 2D Mater. 2, 035002 (2017).

40. Yu, H., Cui, X., Xu, X. & Yao, W. Valley excitons in two-dimensional semiconductor materials. Nat. Sci. Rep. 7, 57–70 (2017).

41. Kormányos, A. et al. k·p theory for two-dimensional transition metal dichalcogenide semiconductors. 2D Mater. 2, 022001 (2015).

42. Lyons, T. P. et al. The valley Zeeman effect in inter- and intra-valley trions in monolayer WSe₂. Nat. Commun. 10, 2330 (2019).

43. Korenev, V. et al. Dynamic spin polarization by orientation-dependent separation in a ferromagnet–semiconductor hybrid. Nat. Commun. 3, 959 (2012).

44. Glazov, M. et al. Exciton fine structure and spin decoherence in monolayers of transition metal dichalcogenides. Phys. Rev. B 89, 201302 (2014).

45. Yu, H., Liu, G.-B., Gong, P., Xu, X. & Yao, W. Dirac cones and Dirac saddle points of bright excitons in monolayer transition metal dichalcogenides. Nat. Commun. 5, 3876 (2014).

46. Maille, M., e Silva, Ed. A. & Sham, L. Exciton spin dynamics in quantum wells. Phys. Rev. B 47, 15776 (1993).

47. Dufferwiel, S. et al. Valley-addressable polaritons in atomically thin semiconductors. Nat. Photonics 11, 497–501 (2017).

48. Jakubczyk, T. et al. Radiatively limited dephasing and exciton dynamics in MoSe₂ monolayers revealed with four-wave mixing microscopy. Nano Lett. 16, 5333–5339 (2016).

49. Godde, T. et al. Exciton and trion dynamics in atomically thin MoSe₂ and WSe₂: Effect of localization. Phys. Rev. B 94, 165301 (2016).

50. Ovesen, S. et al. Interlayer exciton dynamics in van der Waals heterostructures. Commun. Phys. 2, 23 (2019).

51. Merkl, P. et al. Ultrafast transition between exciton phases in van der Waals heterostructures. Nat. Mater. 18, 691–696 (2019).

52. Froehlicher, G., Lorch, S. & Berciaud, S. Charge versus energy transfer in atomically thin graphene-transition metal dichalcogenide van der Waals heterostructures. Phys. Rev. X 8, 011007 (2018).

53. Selig, M., Malic, E., Ahn, K. J., Koch, N. & Knorr, A. Theory of optically induced Förster coupling in van der Waals coupled heterostructures. Phys. Rev. B 99, 035420 (2019).

54. Zhu, C. et al. Exciton valley dynamics probed by Kerr rotation in WSe₂ monolayers. Phys. Rev. B 90, 161302 (2014).

55. Jagla, E. A. Hysteresis loops of magnetic thin films with perpendicular anisotropy. Phys. Rev. B 72, 094406 (2005).

56. Riedl, P. & Zandit-Mangion, I. Difference between domain wall motion in single crystal and polycrystalline YIG observed by pulsed NMR. Phys. Status Solidi A, Appl. Res. 87, K163–K166 (1985).

57. Jeudy, V., Pardo, R. D., Torres, W. S., Bustingorry, S. & Kotlon, A. Pinning of domain walls in thin ferromagnetic films. Phys. Rev. B 98, 054406 (2018).

58. Catarina, G., Peres, N. & Fernández-Rossier, J. Magneto-optical Kerr effect in spin split two-dimensional massive Dirac materials. 2D Mater. 7, 065011 (2020).

59. Thiel, L. et al. Probing magnetism in 2D materials at the nanoscale with single-spin microscopy. Science 364, 973–976 (2019).

60. Matricardi, V., Lehmann, W., Kitamura, N. & Silcox, J. Electron microscope observations of ferromagnetic domains in chromium tribromide. J. Appl. Phys. 18, 127–129 (1967).

61. Virot, F., Favre, L., Hayn, R. & Kuz'min, M. Theory of magnetic domains in uniaxial thin films. J. Phys. D: Appl. Phys. 45, 405003 (2012).

62. Kuhlow, B. & Lambeck, M. Magnetic domain structures in CrBr₃. Physica B +C. 80, 365–373 (1975).

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Author contributions
T. P. L. and D.G. carried out photoluminescence experiments. T.P.L., P.S.K., and F.W. carried out Kerr effect experiments. A.M.S. and J.F.-R. carried out density functional theory calculations. T.P.L., D.G., and A.I.T. analyzed the experimental data. A.M., F.W., and A.K. fabricated the samples. T.T. and K.W. synthesized high-quality hexagonal boron nitride crystals was supported by the Elemental Strategy Initiative conducted by the MEXT, Japan, and the CREST (JPMJCR15F3), JST.

Competing interests
The authors declare no competing interests.

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