Asymmetric magnetic proximity interactions in MoSe$_2$/CrBr$_3$ van der Waals heterostructures

Junho Choi$^{1,2}$, Christopher Lane$^{3,4}$, Jian-Xin Zhu$^{3,4}$ & Scott A. Crooker$^{1,5}$

Magnetic proximity interactions between atomically thin semiconductors and two-dimensional magnets provide a means to manipulate spin and valley degrees of freedom in non-magnetic monolayers, without using applied magnetic fields$^{1–3}$. In such van der Waals heterostructures, magnetic proximity interactions originate in the nanometre-scale coupling between spin-dependent electronic wavefunctions in the two materials, and typically their overall effect is regarded as an effective magnetic field acting on the semiconductor monolayer$^{4–8}$. Here we demonstrate that magnetic proximity interactions in van der Waals heterostructures can in fact be markedly asymmetric. Valley-resolved reflection spectroscopy of MoSe$_2$/CrBr$_3$ van der Waals structures reveals strikingly different energy shifts in the K and K’ valleys of the MoSe$_2$ due to ferromagnetism in the CrBr$_3$ layer. Density functional calculations indicate that valley-asymmetric magnetic proximity interactions depend sensitively on the spin-dependent hybridization of overlapping bands and as such are likely a general feature of hybrid van der Waals structures. These studies suggest routes to control specific spin and valley states in monolayer semiconductors$^{9,10}$.

The ability of short-range proximity interactions to imbue magnetic functionality into otherwise non-magnetic materials$^{20,32}$ has exciting prospects for devices that combine the optical and electrical properties of monolayer semiconductors$^{20–22}$ with additional tuning parameters that couple directly to spin and valley pseudospin$^{33}$. The atomically smooth surfaces that are nowadays routinely achieved with van der Waals (vdW) materials allow for nearly ideal interfaces between monolayer transition metal dichalcogenide semiconductors (such as WSe$_2$ or MoS$_2$) and magnetic substrates (such as EuO or CrI$_3$). Theoretical studies along these lines$^{19–22}$ have been validated by experiments demonstrating, for example, enhanced valley splitting of WSe$_2$ and WS$_2$ monolayers on ferromagnetic EuS$^{24,34}$, and zero-field valley splitting of molybdenum diselenide (MoSe$_2$) monolayers on ferromagnetic chromium bromide (CrBr$_3$) (ref. 35). In parallel, magnetic proximity interactions (MPIs) have also been shown to manifest as spin-dependent charge transfer and concomitant polarized photoluminescence in hybrid devices based on both CrI$_3$(refs. 36) and CrBr$_3$(ref. 37). In studies that measured the overall valley splitting of the A-exciton optical transition, the strength of the MPI could be characterized by an effective magnetic field $B_{\text{eff}}$, typically on the order of 10 T, acting on the semiconductor monolayer$^{38,39}$.

While the notion of an overall effective field $B_{\text{eff}}$ is certainly convenient for characterizing MPIs, it obscures the very real possibility that the effects on spin-up and spin-down bands in the non-magnetic monolayer (or equivalently, effects in the K and K’ valleys) could be substantially different in magnitude. Indeed, given that MPIs originate in the spin-dependent coupling between the underlying electronic band structures of the proximal materials and that ferromagnets typically possess spin-polarized band structures, there is no a priori reason to expect that the influence on the K and K’ valleys should be equal and opposite, as it is for the case of real applied magnetic fields.

$^1$National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM, USA. $^2$Semiconductor Integrated Metrology Team, Korea Research Institute of Standards and Science, Daejeon, Republic of Korea. $^3$Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA. $^4$Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM, USA. $^5$e-mail: crooker@lanl.gov
Bz a confocal microscope probe and loaded into the variable-temperature...

The structures were assembled on Si substrates, mounted on...

...exhibiting out-of-plane ferromagnetic order below its Curie tempera-

ture. The MoSe₂ monolayer was placed on few-layer... by standard dry transfer techniques (Methods). The MoSe₂ monolayer was placed on few-layer CrBr₃ and sandwiched between hexagonal boron nitride (hBN) slabs to exhibit a hBN-encapsulated heterostructure.

K′ valleys of the MoSe₂ are very different in magnitude. Density func-
tional calculations support these findings and indicate that strongly asymmetric MPIs originate from the spin-dependent hybridization of closely overlapping bands in the proximal layers, and are likely a general feature of such hybrid systems.

Figure 1a, b shows an example of a MoSe₂/CrBr₃ heterostructure used in this study. All individual layers were mechanically exfoliated and stacked within an argon glove box using standard dry transfer techniques (Methods). The MoSe₂ monolayer was placed on few-layer CrBr₃ and sandwiched between hexagonal boron nitride (hBN) slabs to maintain high optical quality. CrBr₃ is a two-dimensional vdW magnet exhibiting out-of-plane ferromagnetic order below its Curie temperature. The structures were assembled on Si substrates, mounted on a confocal microscope probe and loaded into the variable-temperature helium insert of a magneto-optical cryostat. Magnetic fields Bz could be applied normal to the sample plane in the Faraday geometry. MCD spectroscopy (depicted in Fig. 1c and described in the Methods) was used to characterize the overall splitting between the K and K′ valleys in the MoSe₂ monolayer, due to MPIs with the CrBr₃ layer. To separately resolve the energy shifts induced at the K and K′ valleys of the MoSe₂, the spectra of right and left circularly polarized reflected light were individually measured.

The presence of strong MPIs in these structures is revealed by the temperature-dependent MCD spectra shown in Fig. 1d. MCD, which detects the intensity difference between right and left circularly polarized light (in reflection or transmission), is inherently sensitive to phenomena that break time-reversal symmetry, such as magnetization. Crucially, all spectra in Fig. 1d were acquired at Bz = 0, after magnetizing the ferromagnetic CrBr₃ along the +ẑ or −ẑ direction. Below the Curie temperature (Tc = 28 K), pronounced MCD signals remain at Bz = 0, at both of the fundamental A- and B-exciton resonances of the MoSe₂ monolayer, indicating the presence of MPIs. Flipping the CrBr₃ magnetization from +ẑ to −ẑ inverts the MCD signals (as expected), and the zero-field MCD signals disappear above Tc. The particular line shapes of the MCD resonances follow the derivatives of the A- and B-exciton resonances as measured in reflection (shown below in Fig. 3).

Figure 1e shows hysteresis loops of the MCD signal, acquired at the peak of the A-exciton resonance, when Bz is varied between ±40 mT, further confirming the MPIs in these heterostructures. These data were taken using a wavelength-filtered xenon lamp, and the focused spot was approximately the same size as the sample itself (~4 μm × 8 μm).

As such, the square hysteresis loops observed at low temperatures indicate that the entire CrBr₃ flake behaves as a single magnetic domain that switches uniformly and is devoid of multi-domain switching phenomena. The hysteresis loops collapse with increasing temperature and disappear above Tc, in line with expectations. The MCD signal versus temperature (T), shown in Fig. 1f, is characteristic of the magnetization of ferromagnetic materials and can be fit to the functional form (1 − T/Tc)β, using Tc = 28 K and β = 0.25 (red line), consistent with...
Spatially resolved images of the MCD over the entire MoSe₂/CrBr₃ heterostructure (Fig. 2) confirm that MPIs are approximately uniform over the entire structure, and that the CrBr₃ layer behaves effectively as a single-domain magnet. For imaging, the probe light was derived from a continuous-wave Ti:S laser, and -1 µm spatial resolution is achieved. MCD images at various applied \( B_z \) around the hysteresis loop show a single domain structure, even near the coercive fields (\( B_z = \pm 15 \text{ mT} \)). MCD images of other vdW heterostructures having thicker CrBr₃ showed a multi-domain magnetic structure near the switching fields, as shown in Extended Data Fig. 2.

Having established the presence of strong MPIs in these hybrid structures, we now turn to the main result: in stark contrast to the influence of real magnetic fields, which shift time-reversed pairs of bands in the K and K’ valleys of MoSe₂ equally and in opposite directions, we find that MPIs in these heterostructures are strongly asymmetric. That is, proximity-induced shifts of the exciton resonances have markedly different magnitudes in the K and K’ valleys. To separately analyze these shifts, we use circular-polarization-resolved, and therefore valley-resolved, optical reflection spectroscopy. (Note that MCD is less sensitive to such asymmetry, since it detects the difference between right and left circular polarization, and not the shift in each valley separately.)

Figure 3a demonstrates this asymmetry. The blue and green traces show the 4 K reflection resonance of the A exciton in the MoSe₂ monolayer, for right and left circularly polarized light, respectively (K’ and K valleys, respectively), when the CrBr₃ is magnetized along the +\( \hat{z} \) direction. To serve as a common reference and control experiment, the red and orange traces were acquired at 30 K (above \( T_c \)), where the CrBr₃ is unmagnetized (and indeed, the red and orange spectra are identical within experimental noise). Clearly, the magnitude of the energy shift at low temperature is noticeably larger in K’ (blue trace) than in K (green trace). This behaviour contrasts with the valley Zeeman shifts arising from real applied magnetic fields, which shift the bands equally and in opposite directions. Importantly, Fig. 3b shows that the left/right circular polarization (K/K’) asymmetry inverts when the CrBr₃ is magnetized along the opposite direction (-\( \hat{z} \)), confirming that the asymmetry is due to MPIs.

The individual energy shifts in the K and K’ valleys can be determined from fits of the reflection resonances to a complex-Lorentzian line shape (Methods) and tracked with good precision. The evolution of the asymmetric energy splitting as a function of temperature is shown in Fig. 3c. The asymmetry exceeds a factor of two, with an energy redshift of ~2 meV in the K’ valley that is accompanied by an opposite blueshift of only ~1 meV in the K valley (for the case of +\( \hat{z} \) CrBr₃ magnetization). The total energy splitting of ~3 meV that is observed at low temperatures is commensurate with the (symmetric) valley splitting expected from a magnetic field of approximately 13 T, assuming a neutral A-exciton Landé g factor \( g_a = 4 \), in very good correspondence with prior work by Ciorciaro et al. We emphasize that the asymmetric shifts are not an artefact of any temperature-dependent bandgap shift arising from the 30 K control spectra; redshifts of the bandgap between 4 K and 30 K are negligible (Extended Data Fig. 3), and furthermore, if present would only make the observed asymmetry even more pronounced.

Interestingly, a rather different asymmetry is observed at the B exciton of MoSe₂, as shown in Fig. 3d. Here, MPIs induce a marked energy shift in the K’ valley (when the CrBr₃ is magnetized along +\( \hat{z} \)) but almost no discernible shift in the K valley. Taken together, we therefore conclude that characterizing the valley splitting by a simple effective magnetic field \( B_{\text{eff}} \) is of limited utility, as it does not capture the marked asymmetry that clearly arises from MPIs. Figure 3e confirms that the K/K’ asymmetry at the B exciton inverts when the CrBr₃ magnetization is flipped, and Fig. 3f shows the evolution of the MPI-induced energy shifts of the B exciton as a function of temperature.

Comparing the energy shifts of the A and B excitons in Fig. 3c-f reveals another unexpected aspect of asymmetric MPIs: for a given CrBr₃ magnetization, the dominant energy shifts for both A- and B-exciton transitions are not only of different sign but also are observed in the same valley. Considering the spin-dependent level structure of the conduction and valence bands in MoSe₂ monolayers (band diagram in Fig. 3), it might be anticipated that a spin-specific proximity

---

**Fig. 2** Spatially imaging MPIs in a MoSe₂/CrBr₃ heterostructure. The ten lower panels show MCD images acquired at 4 K using 1.642 eV probe light (that is, at the A exciton of MoSe₂) at different applied fields \( B_z \) around a typical magnetic hysteresis loop (top). The red dashed line shows the MoSe₂/CrBr₃ heterostructure region. The square hysteresis loop and MCD images indicate that the CrBr₃ behaves as a single magnetic domain. MCD images from a different MoSe₂/CrBr₃ structure are shown in Extended Data Fig. 2.
interaction affecting (for example) only the spin-up bands should cause shifts in the K valley of the A exciton and in the K’ valley of the B exciton. These data demonstrate that the coupling between the electronic band structures of the two constituent materials is more complex.

To provide insight into the asymmetric valley shifts driven by MPIs, we examined the electronic band structure of monolayer MoSe2 stacked on a single layer of CrBr3 (Fig. 4a) within the framework of density functional theory (DFT; Methods). To most directly compare the MPI-induced energy shifts with experimental data (which includes control measurements in the non-magnetic phase of CrBr3), we considered two cases: (1) CrBr3 with out-of-plane ferromagnetic order, to capture the low-temperature phase, and (2) CrBr3 with an in-plane antiferromagnetic spin configuration, to simulate the high-temperature non-magnetic state and serve as a reference. We note that since the band energies are sensitive to the overall electronic environment and band alignment between the CrBr3 and MoSe2 layers (for example, Fig. 4b or Extended Data Fig. 5), one cannot simply compare the band shifts with and without the CrBr3 layer due to intrinsic interlayer coupling even in the non-magnetic phase.

Figure 4c shows the calculated shifts of the optical transition energies in the K and K’ valleys due to MPIs as a function of band alignment between the MoSe2 and CrBr3 layers (controlled by the Hubbard on-site interaction potential, U; Methods), with the experimental values shown by horizontal lines. Most importantly, valley shifts with marked asymmetry are clearly predicted at both the fundamental A and B optical transitions, with overall magnitudes in the range of 1–3 meV, which is in good qualitative agreement with our valley-resolved reflection measurements. We emphasize that these calculations even at the DFT level therefore already capture the essential trends and marked asymmetries shown in the experimental data. However, we note that quantitative agreement with all measurements at the millielectron-volt scale is not universally obtained: for example, using U = 0.9 eV (indicated by the dotted vertical line) yields the correct CrBr3 bandgap and accurately reproduces the measured valley shifts at the B exciton but only qualitatively captures the valley asymmetry at the A exciton. Further refinements to the DFT calculations, beyond the scope of this work, may be obtained by employing self-energy quasiparticle corrections and calculating the full exciton spectrum within the Bethe–Salpeter equation framework.

The asymmetric valley splittings due to MPIs can be understood as follows. Due to the band alignment between the CrBr3 and MoSe2 layers, the conduction states of both layers directly overlap and hybridize, as indicated by the weaker band features in the MoSe2 projected dispersions shown in Fig. 4b. Extended Data Fig. 5 explicitly shows the electronic band projections for both the CrBr3 and MoSe2 layers revealing the substantial mixing between the electronic states of the layers. This hybridization drives resonant avoided-crossing phenomena between same-spin bands, thereby producing strong band shifts, with magnitude and sign sensitively dependent on the detailed alignment of the constituent levels.
Fractional weights of the spin-up (spin-down) MoSe₂-layer projection in the MoSe₂/CrBr₃ heterostructure, with CrBr₃ in the ferromagnetic phase and magnetized along the in-plane b axis. Here, the two monolayers are stacked such that the magnetic chromium sites sit directly below a molybdenum or a selenium atom of MoSe₂ (AA stacking). The unfolded electronic band structure of the MoSe₂/CrBr₃ heterostructure, with CrBr₃ in the ferromagnetic phase and magnetized along +z. The size of the red (blue) dots is proportional to the fractional weights of the spin-up (spin-down) MoSe₂ layer projection in the unfolded Brillouin zone. Calculated energy shifts (ΔE) of the A- and B-exciton transition energies in the ferromagnetic phase of CrBr₃ (with Cr spins oriented ‘up’) relative to a planar-antiferromagnetic state, over a wide range of Hubbard on-site interaction potential U (adjusting U shifts the CrBr₃ bands with respect to the MoSe₂ bands). The planar-antiferromagnetic reference phase is used as an analogue to the experimental high-temperature non-magnetic phase of CrBr₃. Calculations on other stacking arrangements are shown in Extended Data Figs. 6–9. Diagrams illustrating the origin of the asymmetric valley shifts due to MPIs. Blue and red arrows indicate the spin of the various bands. The polarized εg bands of CrBr₃, (represented here by a single level), which are very close in energy to the MoSe₂ conduction bands, primarily repel the like-spin conduction bands of MoSe₂, leading to K/K’ asymmetry. The magnitude and sign of the shifts, indicated by black arrows, depend sensitively on the relative alignment of the layers.

**Figure 4d** shows very simplified illustrations that highlight the essential physics. Like-spin MoSe₂ conduction bands shift to avoid the spin-polarized εg bands of ferromagnetic CrBr₃ (which may be aligned below, between or above the MoSe₂ conduction bands as depicted), yielding valley-dependent shifts of the optical transitions that differ qualitatively from a picture of simple Zeeman splitting. All three scenarios are likely at play due to the presence of multiple εg bands in CrBr₃ (Fig. 4b). Due to the avoided-crossing behaviour, the calculated band shifts have magnitude and sign that depend sensitively on the relative energies of the upper CrBr₃ bands and the MoSe₂ conduction bands, which marks a distinct departure from the effective magnetic field characterization typically employed to quantify MPIs. This behaviour is directly seen as peaks and troughs in the calculated shifts (Fig. 4c), marking the energies at which different CrBr₃ states cross the MoSe₂ bands. (Note that the MoSe₂ valence bands at K and K’ display an approximately symmetric valley splitting, as expected since they do not closely overlap with any states of the CrBr₃ layer.)

Extended Data Figs. 6–9 demonstrate how, within our DFT approach, the calculated energy shifts and the degree of asymmetry evolve for different stacking arrangements of the constituent CrBr₃ and MoSe₂ layers, for various band alignments. These results also suggest that the band alignment and interlayer coupling of a given magnetic heterostructure may be quantified by the experimentally measured sign and magnitude of asymmetric valley shifts. The extent to which twist angle between the MoSe₂ monolayer and the CrBr₃ affects the valley shifts in such hybrid structures has not been explored here, and remains an open question.

By revealing the marked spin/valley asymmetries that can arise from MPIs in a switchable and non-volatile hybrid vdW structure, this work suggests routes towards selective control over specific spin and/or valley states in monolayer transition metal dichalcogenide semiconductors via rational design of the component materials, and also their stacking arrangement. Together with the additional tunability of MPIs that can arise from electrostatic gating (as demonstrated in graphene-based hybrid vdW heterostructures), and recent predictions of gate-tunable band topology in monolayer semiconductors, these results complement the set of available tools with which future spin- and valley-dependent (opto)electronic devices may be engineered. Moreover, our experimental data and DFT calculations strongly indicate that asymmetric MPIs are likely a universal aspect of hybrid vdW heterostructures, manifesting especially in material combinations where electronic bands overlap closely in energy.

**Online content**

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41563-022-01424-w.

**References**

1. Žutić, I., Matos-Abiague, A., Scharf, B., Dery, H. & Belashchenko, K. Proximitized materials. *Mater. Today* **22**, 85–107 (2019).

2. Gibertini, M., Koperski, M., Morpurgo, A. F. & Novoselov, K. S. Magnetic 2D materials and heterostructures. *Nat. Nanotechnol.* **14**, 408–419 (2019).

3. Mak, K. F., Shan, J. & Ralph, D. Probing and controlling magnetic states in 2D layered magnetic materials. *Nat. Rev. Phys.* **1**, 646–661 (2019).

4. Zhao, C. et al. Enhanced valley splitting in monolayer WS₂ due to magnetic exchange field. *Nat. Nanotechnol.* **12**, 757–762 (2017).

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

6. Norden, T. et al. Giant valley splitting in monolayer WS₂ by magnetic proximity effect. *Nat. Commun.* **10**, 4163 (2019).

7. Ciorciaro, L., Kroner, M., Watanabe, K., Taniguchi, T. & Imamoglu, A. Observation of magnetic proximity effect using resonant...
optical spectroscopy of an electrically tunable MoSe2/CrBr3 heterostructure. Phys. Rev. Lett. 124, 197401 (2020).
8. Zhong, D. et al. Layer-resolved magnetic proximity effect in van der Waals heterostructures. Nat. Nanotechnol. 15, 187–191 (2020).
9. Xiao, D., Liu, C.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS2, and other group-VI dichalcogenides. Phys. Rev. Lett. 108, 196802 (2012).
10. Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. Nat. Phys. 10, 343–350 (2014).
11. Lazić, P., Belashchenko, K. D. & Žutić, I. Effective gating and tunable magnetic proximity effects in two-dimensional heterostructures. Phys. Rev. B 93, 241401(R) (2016).
12. Xu, J. et al. Spin inversion in graphene spin valves by gate-tunable magnetic proximity effect at one-dimensional contacts. Nat. Commun. 9, 2869 (2018).
13. Mak, K. F. & Shan, J. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. Nat. Photon. 10, 216–226 (2016).
14. Wang, Q. et al. Excitons in atomically thin transition metal dichalcogenides. Rev. Mod. Phys. 90, 021001 (2018).
15. Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 7, 699–712 (2012).
16. Schailley, J. R. et al. Valleytronics in 2D materials. Nat. Rev. Mater. 1, 16055 (2016).
17. Qi, J., Li, X., Niu, Q. & Feng, J. Giant and tunable valley degeneracy splitting in MoTe2. Phys. Rev. B 92, 121403(R) (2015).
18. Zhang, Q., Yang, S. A., Mi, W., Cheng, Y. & Schwingenschlägl, U. Large spin-valley polarization in monolayer MoTe2 on top of EuO(111). Adv. Mater. 28, 959–966 (2016).
19. Scharf, B., Xu, G., Matos-Abiague, A. & Žutić, I. Magnetic proximity effects in transition-metal dichalcogenides: converting excitons. Phys. Rev. Lett. 119, 127403 (2017).
20. Zollner, K., Faria, P. E. Jr & Fabian, J. Proximity effects in MoSe2 and WSe2 heterostructures with CrI3: twist angle, layer, and gate dependence. Phys. Rev. B 100, 085128 (2019).
21. Zhang, Z., Ni, X., Huang, H., Hu, L. & Liu, F. Valley splitting in the van der Waals heterostructure WSe2/CrI3: the role of atom superposition. Phys. Rev. B 99, 115441 (2019).
22. Xie, J., Jia, L., Shi, H., Yang, D. & Si, M. Electric field mediated large valley splitting in the van der Waals heterostructure WSe2/CrI3. Jpn. J. Appl. Phys. 58, 010906 (2019).
23. Lyons, T. P. et al. Interplay between spin proximity effect and charge-dependent exciton dynamics in MoSe2/CrBr3, van der Waals heterostructures. Nat. Commun. 11, 6021 (2020).
24. Chen, W. et al. Direct observation of van der Waals stacking-dependent interlayer magnetism. Science 366, 983–987 (2019).
25. Kim, H. H. et al. Evolution of interlayer and intralayer magnetism in three atomically thin chromium trihalides. Proc. Natl Acad. Sci. USA 116, 11131–11136 (2019).
26. Soriano, D., Katsnelson, M. I. & Fernandez-Rossier, J. Magnetic two-dimensional chromium trihalides: a theoretical perspective. Nano Lett. 20, 6225–6234 (2020).
27. Fisher, M. E. The renormalization group in the theory of critical behavior. Rev. Mod. Phys. 46, 597–616 (1974).
28. Stier, A. V., McCreary, K. M., Jonker, B. T., Kono, J. & Crooker, S. A. Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS2 and MoS2 to 65 Tesla. Nat. Commun. 7, 10643 (2016).
29. Xu, G., Zhou, T., Scharf, B. & Žutić, I. Optically probing tunable band topology in atomic monolayers. Phys. Rev. Lett. 125, 157402 (2020).
Methods
Sample preparation
Monolayer MoSe₂ (2D Semiconductors) and hBN flakes were mechanically exfoliated from bulk crystals onto Si substrates under ambient conditions and moved into an Ar glove box, where O₂ and H₂O concentrations were maintained below 0.1 ppm. Few-layer flakes of CrBr₃ (HQ Graphene) were exfoliated onto Si substrates inside the glove box. MoSe₂/CrBr₃ heterostructures were assembled by standard dry transfer techniques using polycarbonate stamps and were sandwiched between hBN slabs. Then the samples were moved out of the glove box and washed in chloroform to remove polymer residues. The thickness of the CrBr₃ (typically five layers) was identified by atomic force microscopy after the polymer residue was removed. The samples were mounted on a confocal microscope probe and mounted in the helium-flow insert of a 7 T superconducting magnet with direct optical access.

MCD spectroscopy and imaging
Broadband MCD spectroscopy was performed in a reflection geometry using wavelength-tunable narrowband light derived from a xenon white light source filtered through a 300 mm spectrometer. The probe light was intensity modulated by mechanical chopper, and then modulated between left and right circular polarizations by a linear polarizer and photoelastic modulator. The light was focused to a small spot (approximately 4 μm × 8 μm) on the sample by an aspheric lens that was controlled by a piezo nanopositioner (Attocube). The back-reflected light from the sample was collected by the same lens and directed by a beam-splitter to an avalanche photodiode detector (as depicted in Fig. 1c). The signal was demodulated by two lock-in amplifiers, referenced to the chopper and photoelastic modulator frequencies (137 Hz and 50 kHz, respectively). MCD is given by the normalized intensity difference between right and left circularly polarized reflected intensities, (I_R − I_L)/(I_R + I_L). For the MCD imaging experiments shown in Fig. 2, the probe light was derived from a tunable continuous-wave Ti:sapphire laser (≈1 μm focused spot size). The incident probe laser beam was coupled to a two-dimensional galvanometer mirror scanner for raster scanning and spatial imaging.

Polarization-resolved and valley-resolved reflection spectroscopy
The polarization-resolved reflection measurements were performed using the same confocal microscope described previously. Here, broadband white light from a Xen lamp was coupled into a single-mode fibre, then collimated by an achromatic lens and then circularly polarized using a linear polarizer and quarter-wave plate. The white light was then focused to a 1 μm spot with an aspheric lens. The reflected light from the sample was collected by a multi-mode fibre and detected by a cooled charge-coupled device (CCD) detector. As is typical for reflection spectroscopy of vdW heterostructures, the A- and B-exciton resonances exhibit a complex-Lorentzian line shape (that is, having both dispersive and absorptive components to the line shape). Once a fit was established at a given temperature, the temperature-dependent shift of the transition energy (Fig. 3) was accurately tracked by fixing all parameters except for the resonance energy. Alternatively, letting all fit parameters float yielded similar results, because the line shape remains unchanged.

DFT calculations
DFT-based first-principles electronic structure calculations were carried out using the pseudopotential projector-augmented wave method implemented in the Vienna Ab initio Simulation Package. We used an energy cut-off of 300 eV for the plane-wave basis set. Exchange–correlation effects were treated using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation density functional. Van der Waals corrections were included following the prescription of Grimme. Our results were further benchmarked against the non-local vdW-DF functional. After adjusting U to account for the different bandgaps obtained by PBE and vdW-DF, we find that both approaches give asymmetric valley splittings, with the same sign structure and similar magnitudes. A 15 × 15 × 1 Γ-centred k-point mesh was used to sample the Brillouin zone. Spin–orbit coupling effects were included self-consistently. An effective Hubbard U was added to the Cr 3d orbitals to control the band alignment and correct the bandgap of the magnetic layer. A U of 0.9 eV was found to yield the experimental bandgap of CrBr₃, and the asymmetric optical transitions simultaneously. We note that PBE outperforms HSE06 in capturing the bandgap of MoSe₂, (ref. 30), where HSE06 exaggerates the fundamental gap of MoSe₂ and CrBr₃ by ~300 meV (ref. 40) and ~500 meV (ref. 40), respectively. In this case, HSE06 reproduces an equivalent band alignment as our PBE + U calculations for U = 1.0 eV. The heterobilayer was constructed from a 1 × 1 unit cell of CrBr₃ and a 2 × 2 supercell of MoSe₂. To not alter the electronic structure of the MoSe₂ layer, we strained CrBr₃ to make both layers commensurate. Three distinct stacking configurations were considered, as shown in the Extended Data figures. To ensure negligible interaction between the periodic images of the bilayer film, a large enough vacuum of ~500 Å in the z direction was used. Finally, all atomic sites in the unit cell were relaxed simultaneously using a conjugate gradient algorithm to minimize energy with an atomic force tolerance of 0.01 eV Å⁻¹ and a total energy tolerance of 10⁻⁶ eV. The unfolded band structure was obtained using the Pyyrocarr package.

Data availability
All data are available from the corresponding author upon reasonable request.

References
30. Kim, K. et al. Van der Waals heterostructures with high accuracy rotational alignment. Nano Lett. 16, 1989–1995 (2016).
31. Robert, C. et al. Optical spectroscopy of excited exciton states in MoS₂, monolayers in van der Waals heterostructures. Phys. Rev. Mater. 2, 011001(R) (2018).
32. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).
33. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).
34. Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. Phys. Rev. B 48, 13115–13118 (1993).
35. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
36. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).
37. Dion, M., Rydberg, H., Schröder, E., Langreth, D. C. & Lundqvist, B. I. Van der Waals density functional for general geometries. Phys. Rev. Lett. 92, 246401 (2004).
38. Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J. & Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA+U study. Phys. Rev. B 57, 1505–1509 (1998).
39. Huang, T. L. et al. Scanning tunneling spectroscopy of van der Waals graphene/semiconductor interfaces: absence of Fermi level pinning. 2D Mater. 4, 035019 (2017).
40. Gusakova, J. et al. Electronic properties of bulk and monolayer TMDs: theoretical study within DFT framework (GVJ-2e method). Phys. Status Solidi A 214, 1700218 (2017).
Acknowledgements

We gratefully acknowledge I. Žutić and B. Urbaszek for helpful discussions. Experimental studies at the National High Magnetic Field Laboratory were supported by the Los Alamos Laboratory Directed Research and Development programme (J.C. and S.A.C.). The National High Magnetic Field Laboratory is supported by National Science Foundation DMR-1644779, the State of Florida and the US Department of Energy. Computational studies were supported in part by the Center for Integrated Nanotechnologies, a US Department of Energy Basic Energy Sciences user facility, in partnership with the Los Alamos National Laboratory Institutional Computing Program for computational resources (C.L. and J.-X.Z.). Additional computations were performed at the National Energy Research Scientific Computing Center, a US Department of Energy Office of Science user facility located at Lawrence Berkeley National Laboratory, operated under contract no. DE-AC02-05CH11231 using National Energy Research Scientific Computing Center award ERCAP0020494.

Author contributions

J.C. and S.A.C. conceived the project. J.C. prepared the samples and performed the optical experiments. C.L. and J.-X.Z. performed the DFT calculations. All authors contributed to writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Extended data is available for this paper at https://doi.org/10.1038/s41563-022-01424-w.

Correspondence and requests for materials should be addressed to Scott A. Crooker.

Peer review information Nature Materials thanks the anonymous reviewers for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.
Extended Data Fig. 1 | Additional MCD data and MCD spectra. a. Hysteresis loops of the MCD signal from the MoSe2/CrBr3 heterostructure, acquired at the B-exciton transition of the MoSe2 monolayer (photon energy = 1.83 eV; cf. Fig. 1e of the main text). b. MCD spectra of an isolated 'control' MoSe2 monolayer, compared with the MCD spectra of the MoSe2/CrBr3 heterostructure, at 4 K. Each spectrum was obtained after the CrBr3 was magnetized by applied magnetic fields (cf. Fig. 1d of the main text).
Extended Data Fig. 2 | MCD images of magnetic proximity effects on a different MoSe₂/CrBr₃ heterostructure. The CrBr₃ thickness is 7 monolayers. **a**, Optical microscope image of the vdW structure. **b**, Magnetic hysteresis of the MCD signal, using light tuned to the A-exciton transition of the MoSe₂ monolayer. **c**, MCD images acquired at 4 K, using probe light tuned to the peak of the A-exciton MCD resonance (photon energy = 1.64 eV), at selected applied magnetic fields $B_z$. The MoSe₂/CrBr₃ heterostructure region is indicated by the black dashed lines, and red and blue colors reveal magnetic domains oriented along $+\hat{z}$ and $-\hat{z}$, respectively. Magnetic domains in CrBr₃ have been studied using a variety of techniques over the past several decades; see for example44,45.
Extended Data Fig. 3 | Reflection spectra from control sample. Reflection spectra from an isolated ‘control’ MoSe$_2$ monolayer (raw data), showing that the energy of the exciton resonance shifts negligibly at the low temperatures ($T \leq 30$ K) considered in this work. Black and red traces were acquired at 6 K and 30 K, respectively.
Extended Data Fig. 4 | Total (not valley-resolved) MPI-induced valley splitting. **a**, The energy difference between the \( K \) and \( K' \) A-exciton resonance energies shown in Fig. 3c of the main text. **b**, The energy difference between the \( K \) and \( K' \) B-exciton resonance energies shown in Fig. 3f of the main text. These plots are shown for completeness — as the main text emphasizes, plotting energy differences obscure the marked valley asymmetry that arises due to MPIs. Error bars represent 95% confidence intervals on the fitting of the resonance energy.
Extended Data Fig. 5 | Calculated electronic band structures. Theoretical electronic band structures for various CrBr₃ magnetic configurations. The unfolded electronic band structure of the MoSe₂/CrBr₃ heterostructure for CrBr₃ ferromagnetically polarized along \( +\hat{z} \) (a-b), \( -\hat{z} \) (c-d), and in the planar-antiferromagnetic phase (e-f). Top and bottom panels show the MoSe₂ and CrBr₃ layer projections, respectively. The sizes of the red (blue) dots are proportional to the fractional weights of the spin-up (down) MoSe₂ and CrBr₃ layer projections, respectively. In the first two columns, the CrBr₃ conduction states clearly cut through the MoSe₂ unoccupied bands, thereby generating substantial level mixing and repulsion. The hybridization between these sets of bands is marked by the pronounced ‘shadow’ of CrBr₃ bands in the MoSe₂ projected states (a,c). In the right-most column (panels e,f), minimal band mixing between the layers is observed. Since the chromium magnetic moments lie in the plane, the electron overlap integrals connecting the CrBr₃ layer and the spin-polarized bands in MoSe₂ are substantially reduced. Furthermore, since there is no net magnetic moment in the planar-antiferromagnetic phase, the valley degeneracy is preserved.
Extended Data Fig. 6 | Crystal structure of MoSe₂/CrBr₃ for various stacking arrangements. The MoSe₂/CrBr₃ bilayer structure viewed from the top for AA, AB and AC stacking configurations. The green, violet, orange and blue spheres denote the selenium, molybdenum, bromine and chromium, respectively. The black line indicates the unit cell boundary.
Extended Data Fig. 7 | Calculated valley shifts vs. U for AA stacking. Calculated shifts of the optical transition energies in the K and K' valleys as a function of U for AA stacked MoSe$_2$/CrBr$_3$. Dashed horizontal lines show experimentally measured values. As the effective Hubbard U on the chromium atomic sites is increased from 0 to 2 eV the optical transition energies in the K and K' valleys (solid lines with dots) display a non-monotonic evolution for both +z and −z chromium spin polarizations. Since the relative band alignment between CrBr$_3$ and MoSe$_2$ states changes with increased U, the resulting resonant avoided crossing phenomena produces a blue or red shift in the optical transition energies. A U = 0.9 eV (denoted by vertical dotted line) is found to simultaneously reproduce the experimental band gap of CrBr$_3$, and qualitatively capture the 1–3 meV magnitude of the asymmetric exciton shifts in the two valleys.
Extended Data Fig. 8 | Calculated valley shifts vs. $U$ for AB stacking. Same as Extended Data Fig. 7, except for AB stacked MoSe$_2$/CrBr$_3$. 
Extended Data Fig. 9 | Calculated valley shifts vs. $U$ for AC stacking. Same as Extended Data Fig. 7, except for AC stacked MoSe$_2$/CrBr$_3$. 