Giant valley splitting in monolayer WS\textsubscript{2} by magnetic proximity effect

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Lifting the valley degeneracy of monolayer transition metal dichalcogenides (TMDs) would allow versatile control of the valley degree of freedom. We report a giant valley exciton splitting of 16 meV/T for monolayer WS\textsubscript{2}, using the proximity effect from an EuS substrate, which is enhanced by nearly two orders of magnitude from that obtained by an external magnetic field. More interestingly, a sign reversal of the valley splitting is observed as compared to that of WSe\textsubscript{2} on EuS. Using first principles calculations, we investigate the complex behavior of exchange interactions between TMDs and EuS. The sign reversal is attributed to competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions for Eu- and S- terminated EuS surface sites. They act differently on the conduction and valence bands of WS\textsubscript{2} compared to WSe\textsubscript{2}. Tuning the sign and magnitude of the valley exciton splitting offers opportunities for control of valley pseudospin for quantum information processing.
Proximity effect in condensed matter physics refers to the extension of a particular order parameter of a material into an adjacent material. A well-known example is the superconductivity proximity effect, which occurs when a superconductor is placed in contact with a nonsuperconducting material. Superconductivity emerges in the normal region over mesoscopic distances. Another example is the magnetic proximity effect, where a magnetic material induces magnetic moment and magnetic order in a nonmagnetic material adjacent to it. As the penetration depth of the magnetic proximity effect is governed by short range exchange interactions, it will be more pronounced in thin film heterostructures, especially in atomically thin 2D heterostructures. Recently, ferromagnetism induced by the interfacial exchange field from a magnetic substrate in graphene and topological insulators has been observed. Magnetic proximity effect has also been used to break the time-reversal symmetry and lift the valley degeneracy in TMDs. Compared to magnetic doping, utilizing the magnetic proximity effect allows us to avoid the introduction of defects and reliably separate bulk from surface state effects.

Monolayer TMDs, such as MoS2, MoSe2, WS2, and WSe2 have attracted great interest in recent years because of their unique optical and electronic properties. The broken inversion symmetry in monolayer TMDs results in two degenerate yet inequivalent valleys at the corners of the hexagonal Brillouin Zone, labeled as K and K’ valleys. The strong spin–orbit coupling leads to spin splitting of the top valence band and bottom conduction band in the two valleys. The spin orientations are opposite in these valleys, due to the time reversal symmetry. This coupling of spin and valley degrees of freedom in monolayer TMDs renders valley dependent optical selection rules, and makes them attractive for spintronics and valleytronics applications.

For valleytronics applications, creating, switching, and detecting valley polarization are required. Transient valley polarization has been achieved by optical excitation and spin injection. Valley pseudospins are useful as qubits since their coherent states can be initialized, controlled, and read out using optical pulses. Lifting the valley degeneracy can lead to robust, nonvolatile valley polarization. This has been done by applying an external magnetic field, as lifting the degeneracy requires breaking the time reversal symmetry. Applying a magnetic field has also been used to rotate the valley exciton pseudospin, a necessity for valley qubits. However, a tiny valley exciton Zeeman splitting of 0.2 meV/T makes valley control difficult at moderate fields. It was found that the valley pseudospin can be rotated by up to 35° at a very large external field of 25 T. Magnetic doping in TMDs to lift the valley degeneracy has also been attempted. However, valley splitting by doping has yet to be demonstrated. Recently, we have shown that, by exploiting the magnetic proximity effect from the ferromagnetic insulator EuS, valley splitting of monolayer WSe2 can be enhanced by more than an order of magnitude. Xu et al. also demonstrated valley splitting and polarization in WSe2/EuS. Both of these results show the possibility to control the valley degree of freedom in a feasible low-magnetic field using magnetic proximity effect.

One of the key differences between exchange induced valley splitting by magnetic proximity effect and Zeeman splitting due to an external field is that while Zeeman splitting is nearly identical in value for different TMDs (~0.2 meV/T) due to their similar electronic structures and the same orbital moment contributions; the exchange valley splitting by magnetic proximity effect, on the other hand, is governed by the strength of the exchange interactions and is thus tunable depending on the types of TMDs and magnetic substrates, their spatial separation and band alignment. Furthermore, unlike Zeeman splitting which always lowers (raises) the energy of spin up (down) states, exchange interactions can be either positive (FM) or negative (AFM), depending on the nature of the interface and interatomic spacing. A natural question arises is then whether one can exploit this aspect of the exchange interaction to tune both the magnitude and sign of valley splitting of TMDs, which is otherwise unattainable by Zeeman effect. To this end, we chose two types of TMDs, namely WS2 and WSe2 with different band gaps and fabricated their heterostructures with ferromagnetic EuS. WS2 and WSe2 are expected to possess different band alignment with EuS and thus different exchange interactions. We then investigated their valley exciton splitting by magneto-reflection measurements.

In this letter, we show that in WS2/EuS, the magnetic proximity effect results in a giant valley exciton splitting, up to two orders of magnitude higher than that obtained from an external magnetic field. Moreover, a sign reversal of the splitting is observed by comparing the behavior of WS2/EuS vs. WSe2/EuS. Using first principles calculations, we elucidate the critical role of the interface, in particular the effects of the competition between different surface terminations on band alignment and the exchange. The possibility to tune not only the magnitude but also the sign of valley splitting offers opportunities to explore new physics, and provides flexibility in valley control for applications in information processing.

Results

Growth and characterizations of monolayer TMDs. Monolayer WS2 and WSe2 were grown by sulfurization and selenization of WO3 thin layers grown by electron beam deposition, following our previously published procedures. They were then transferred onto magnetic EuS and nonmagnetic Si/SiO2 substrates. The morphologies were studied by optical, scanning electron, and atomic force microscopies. Raman and photoluminescence spectroscopies measured at room temperature were used to confirm their monolayer character.

Figure 1a shows the optical microscope image of the as-grown monolayer WS2 on sapphire substrate (the inset is a SEM image). As shown in the image, each single crystal is of regular triangular shape with a size of 10–20 µm. Figure 1b, c is the corresponding reflection and transmission images. The separation between these two peaks is 59.4 cm⁻¹, consistent with reported value for monolayer WS2. After being transferred onto SiO2 and EuS substrates, respectively. We can see that the transfer process does not lead to change in morphology. In Fig. 1d–i, Raman spectra of the WS2 films on sapphire, SiO2, and EuS substrates are shown. For the sample on sapphire substrate, the E2g and A1g phonon features have Raman shifts of 355.3 and 414.7 cm⁻¹. The separation between these two peaks is 59.4 cm⁻¹, consistent with reported value for monolayer WS2. After being transferred onto SiO2 and EuS substrates, the separation changes to 62.5 and 62.4 cm⁻¹, which may be associated with the chemical bonding between the WS2 and SiO2 and EuS substrates. The PL peak energy is at 626 nm (1.98 eV) (Fig. 1g), which can be attributed to the A exciton transition. The PL peak values change slightly to 616.4 nm (2.01 eV) and 620.9 nm (2.00 eV) for samples on SiO2 and EuS substrates (Fig. 1h, i). These values are consistent with values reported previously for monolayer WS2.

Magneto-reflection measurements of valley exciton splitting. Temperature dependent magneto-reflection measurements were performed in the Faraday geometry to determine the valley exciton splitting of TMDs. In this geometry, the optical beam is parallel to the magnetic field and perpendicular to the sample. A linear polarizer and a Babinet–Soleil compensator was used to generate left and right circularly polarized light (Supplementary Fig. 1).
Figure 2a, c shows the reflectance spectra of monolayer WS2 on Si/SiO2 substrate, measured at 7 K and a magnetic field of 0 and 7 T, respectively. While Fig. 2b, d shows the reflectance spectra of WS2 on ferromagnetic EuS substrate measured at identical conditions. The vertical axis labeled as $R/R_0$ represents the ratio between the reflectance of WS2 and either Si/SiO2 or EuS substrate background. A complex (absorptive + dispersive) Fano line shape was used to fit the reflectance spectra to extract the transition energies (Supplementary Fig. 2 and Supplementary Note 1). The local minima were found to be ~2.1 eV, corresponding to the A exciton transition energy. In all figures, the left (right) circularly polarized light, denoted as $\sigma^+$ ($\sigma^-$), corresponds to the inter-band transition at the $K$ ($K'$) valley. As can be seen from the top panels in Fig. 2a, b, at zero field, the $\sigma^+$ and $\sigma^-$ spectra match well with each other, confirming the degeneracy of the two valleys. When a + 7 T magnetic field is applied, however, an energy shift of the exciton transition is observed for WS2 on both Si/SiO2 and EuS substrates (Fig. 2c, d). The $\sigma^+$ spectrum shifts to lower energy, while the $\sigma^-$ spectrum shifts to higher energy for WS2 on Si/SiO2. While spin, atomic orbital, and valley orbital magnetic moments all contribute to the Zeeman shift of the valley states\textsuperscript{35–29}, it is understood that the valley exciton splitting, which is the difference between the exciton transition energies in the K and K' valleys defined as $\Delta E \equiv E(\sigma^-) - E(\sigma^+)$, is dominated by the atomic orbital moment of the top valence band at the K and K' valleys, each contributing $2\mu_B$ and $-2\mu_B$, respectively\textsuperscript{14,25,26,28,29}. The Zeeman splitting of the valley exciton is thus $\Delta E = 4\mu_B B$, where B is the applied magnetic field. The valley splitting of WS2 on Si/SiO2 is measured to be 1.5 meV at 7 T, consistent with the prediction and the values reported earlier\textsuperscript{28,29}. For WS2 on EuS, however, unexpected behaviors are observed. As can be seen from Fig. 2d, the separation between the $\sigma^+$ and $\sigma^-$ spectra is much larger, i.e., a much larger valley exciton splitting. Moreover, the sign of valley exciton splitting is reversed, with $\sigma^+$ spectrum shifting to higher energy while $\sigma^-$ shifting to lower energy. The sign of $\Delta E$ is also opposite to that of WSe2/EuS reported by us previously\textsuperscript{11}. This sign reversal suggests interesting physics associated with the magnetic proximity effect that are qualitatively different from the Zeeman effect.

To elucidate the origin of the valley exciton splitting induced by the EuS substrate, we measured and plotted in Fig. 3a $\Delta E$ of WSe2 as a function of the applied magnetic field for monolayer WS2 on EuS and SiO2, respectively. We also plot the data of monolayer WSe2 on EuS for comparison. There are clear contrasting behaviors in the dependence of $\Delta E$ on B. For WS2 on SiO2, $\Delta E$ increases linearly with increasing magnetic field at a slope of ~0.2 meV/T (Fig. 3a, red dots), consistent with a g-factor
of ~4. As for WS2 on EuS, ΔE vs. B shows prominent nonlinear behavior, with an initial slope of −16 meV/T at |B| < 1 T (for WSe2 on EuS, the slope is +2.5 meV/T). The magnitude of ΔE for WS2/EuS corresponds to a g-factor of −320, which is nearly two orders of magnitude higher than that on Si/SiO2 substrate and 7 times higher than the value of WSe2/EuS. This giant enhancement in valley exciton splitting clearly originates from the interactions between the monolayer WS2 and the magnetic EuS substrate. ΔE of WS2/EuS saturates at fields above 3 T, with a magnitude of 19 meV.

If the valley splitting originates from the magnetic proximity effect, ΔE of WS2 as a function of B field should follow the trend of the out-of-plane magnetization of EuS, as \( B_{ex} \propto S_z \) [11]. To verify this, the field dependent valley exciton splitting of WS2/EuS and the out-of-plane magnetic hysteresis loops of the EuS film were measured at identical temperatures ranging from 7 to 50 K, and plotted in Fig. 3b. A linear background of 0.2 meV/T is subtracted to reveal the net contribution from MEF, which is denoted as ΔE_{ex}. ΔE_{ex} and the magnetization M are normalized by their saturated values at 7 K, respectively, and the sign of the magnetization is inverted so that the two sets of data can be conveniently compared. EuS is a soft magnetic material with its easy axis in the plane. As can be seen from Fig. 3b, the hysteresis loop shows negligible remnant magnetization, and saturates at approximately 2 T at 7 K. With increasing temperature, the saturation magnetization decreases accordingly. As T increases to 50 K, M becomes approximately linear. EuS has a Curie temperature \( T_C \) of 16.7 K, and is expected to be paramagnetic at 50 K. However, the EuS film at 50 K shows a magnetic susceptibility larger than that expected for a typical paramagnetic material, suggesting some residual ferromagnetic correlation. As for valley exciton exchange splitting, at 7 K, ΔE_{ex} increases rapidly with increasing field for |B| < 1 T; above 1 T, ΔE_{ex} increases slowly and then tends toward saturation at higher fields. With increasing temperature, the saturated value of ΔE_{ex} decreases. As T further increases to 50 K, ΔE_{ex} shows approximately linear field dependence with a slope of −0.4 meV/T. As the nonmagnetic background has already been subtracted, this value reflects the contribution from MEF of the EuS substrate. The field-dependence of ΔE_{ex} is observed to be closely mimicking the behavior of magnetization at different measurement temperatures, as can be seen from Fig. 3b. This unambiguous correlation between valley exciton splitting for WS2 and out-of-plane magnetization of EuS clearly establishes the MEF
as the origin of valley splitting. The sign reversal of valley splitting, however, reflects the complicated behavior of exchange interactions, which remains to be understood. Below we show calculation results of electronic structure for WSe$_2$/EuS and WS$_2$/EuS, and extract band edge energies at $K$ and $K'$ points of the Brillouin Zone using density functional theory (DFT), to explain the observed intriguing behavior of valley exciton splitting.

Exchange coupling between the EuS substrate and TMDs occurs predominantly between states of transition metal (Mo, W) and magnetic surface atom (Eu in our case). The exchange interactions are of indirect exchange-type mediated by nonmagnetic chalcogen elements. The situation is different from the conventional superexchange picture where exchange is considered between two transition metal cations mediated by a nonmagnetic anion. Eu possesses large localized $f$-state magnetic moment. Its $d$-orbitals (partially populated with ~0.4 $\mu_B$) by the core $f$-electrons and, thus, the exchange is indirect. Nevertheless, the magnitude and sign of exchange interactions depend sensitively on the interface structure, i.e., interatomic distances and termination of the surface.

**Structural model for DFT calculations.** Due to the hexagonal structure of TMDs, it is not possible to construct a perfectly lattice matched interface between TMD and EuS. For example, (100) and (011) surfaces of cubic systems do not match by symmetry, while (111) surface of EuS does not match due to large difference in lattice parameters. Furthermore, (111) surface for EuS and many other cubic systems is polar, and reconstruction inevitably occurs to avoid the polar catastrophe. In most earlier theoretical calculations, a (111) polar surface was assumed$^{9,10}$. This leads to strong electrostatic interaction between TMD and the magnetic substrate, reducing the interlayer distance and promoting the exchange interactions. The calculated valley exciton exchange splitting was often orders of magnitude larger than experimental observations$^{9,10}$.

The realistic surface of an EuS thin film may not have a (111) surface terminated simply by either Eu or S because of the polarity issue. Thus, the surface is expected to have about the same number of surface Eu and S sites (which is true for (100) and (110) high symmetry terminations). The TMD deposited on EuS in this case will have nearly the same distance to the surface S and Eu sites. For monolayer WSe$_2$ or WS$_2$, the exchange coupling between W and Eu sites will then be mediated either by single S/Se site in TMD or double chalcogenide bridge as shown in Fig. 4. If indirect exchange favors AFM coupling for a single chalcogenide bridge, the interaction for the double chalcogenide bridge would be FM and vice versa. In considered layered systems, exchange interactions should depend strongly on the surface atom arrangements and interlayer distance, as well as surface polarity. W has less than half-filled 4$d$ shell and should have FM indirect exchange and its magnitude is expected to decrease with increasing distance. The average of the exchange effects from Eu- and S-terminated surfaces should give reasonable expectation values of the net substrate effects.

The structural model constructed for EuS (111) polar surface have relatively low mismatch with monolayers of WS$_2$ and WSe$_2$, which have lattice constants of 3.148 and 3.316 Å, respectively. The lattice parameter of EuS is 5.97 Å and it has rock salt structure, making the in-plane lattice constant of (111) surface of EuS ~4.44 Å. Using $\sqrt{3}\times\sqrt{3}$ construction of unit cell we can reduce the lattice constant to ~7.3 Å. Because TMDs are not expected to have large strain in the experimentally deposited systems, we have kept lattice parameter of the supercell equal to equilibrium lattice parameters of WS$_2$ or WSe$_2$. This induces relatively large strain in EuS lattice; however, it is sufficient to explore the effect of the substrate on the electronic states of TMDs. We considered Eu-terminated and S-terminated EuS surfaces that is shown schematically in Fig. 4.

Figure 4 shows that the exchange field effect between magnetic Eu- and W-states is mediated by the nonmagnetic chalcogen element. For WS$_2$, the interaction between Eu and W states is mediated by S for Eu-terminated surface (single S bridge), while Eu–S–S–W (double S–S bridge) is present for the case of S-terminated surface. For WSe$_2$, the interaction between Eu and W states is mediated by Se for Eu-terminated surface (single Se bridge), while Eu–S–Se–W (double S–Se bridge) is present for the case of S-terminated surface.

**Results of DFT calculations.** Our calculation shows that depending on the termination of EuS surface (Eu vs. S), the Eu–W distance varies significantly (Table 1).

In our calculations, we kept the distances between TMD and the surface equal for both Eu and S terminations because the realistic surface should have mixture of S and Eu terminations to remove the polarity. In this case the TMD monolayer will be planar and keep nearly the same distance for either termination. This distance was chosen to be the relaxed spacing calculated for Eu-terminated surface (2.76–2.77 Å), due to the stronger electrostatic interactions between the Eu sites and chalcogen elements in TMDs. Thus, the discussion of the differences and similarities of TMD properties deposited on EuS will be the most consistent.

**Eu-terminated (111) polar surface.** Overall, WS$_2$ on the polar Eu-terminated EuS surface shows behavior similar to that of WSe$_2$,$^{11}$ as seen in band structure plots in Fig. 5a, c, and projected partial density of states (DOS) in Fig. 6a, c. Due to the electrostatic attraction between the surface Eu and S sites, there is a significant redistribution of the charges in WS$_2$ (WSe$_2$) and dipole moment forms at the interface. The Fermi energy falls into the conduction band and is likely due to the polarity of the interface.

**Table 1 Calculated equilibrium interlayer distances for polar surfaces of WS$_2$ and WSe$_2$ on EuS**

|          | Eu-terminated (Å) | S-terminated (Å) |
|----------|-------------------|------------------|
| WS$_2$   | 2.76              | 3.19             |
| WSe$_2$  | 2.77              | 3.21             |
**Fig. 5** Band structure. Band structure of WS$_2$ (a, b), and WSe$_2$ (c, d). Left panel: Eu-terminated EuS, right panel: S-terminated EuS. The W d-states are shown as red (spin-up) and blue (spin-down) bands. Notice that the shifts of the valence and conduction bands in cases of Eu- and S-terminations are in opposite directions due to the opposite polarity.

**Fig. 6** Density of states. Partial densities of states of surface Eu (black) and W (red) of WS$_2$/EuS and WSe$_2$/EuS for polar surface of EuS: a WS$_2$/EuS terminated by Eu atoms; b WS$_2$/EuS terminated by S atoms; c WSe$_2$/EuS terminated by Eu atoms; and d WSe$_2$/EuS terminated by S atoms. (Upper half of the plots-majority, lower half of the plots-minority). Fermi energy is placed at zero and marked by dashed vertical line.
The band structure shows considerable shift in conduction and valence bands due to the presence of the EuS substrate. As can be seen from Fig. 6a, c, the conduction band edge of WS₂ (WSe₂) (red) aligns with that of EuS (black) and causes large exchange splitting between the majority and minority states of TMDs. The on-site exchange splitting is about 0.2–0.3 eV, noticeable in the shift of the DOS seen in Fig. 6a, c. Note that one should differentiate the edge of the conduction bands from the W-d states responsible for optical transitions. This can be seen clearly from Fig. 5a, c. Labeled by the circle in Fig. 5a are the conduction band edge states with large exchange splitting between the majority and minority states. They are dominated by interfacial S states that are hybridized with W-states. On the other hand, the edge of the valence states has substantially smaller exchange splitting due to the different character of the bands that is made up mainly of W-d states (Fig. 5a, c), and there is no interface related states at this energy window. As a result, the interfacial states in the conduction band do not contribute to exciton intensity. The distinguishing feature of such a system is the presence of spin polarization in WS₂ (WSe₂) resulting in finite magnetic moments of about 0.1 μB/f.u. This induced moment is significant and should be detectable by X-ray magnetic circular dichroism.

On the other hand, the bottom of the W-d states in the conduction band responsible for the optical transition is located above the conduction band edge. The spin-resolved bands for W-d states are shown in Fig. 5 in red and blue color for majority and minority states, respectively. These states exhibit a spin state inversion between K- and K’-high symmetry points of the Brillouin zone and are responsible for exciton optical spectra. The on-site exchange splitting of 0.2–0.3 eV is nearly an order of magnitude larger than the exchange shift of W-d states (~0.04 eV). Note that it is the difference in the exchange shift of W-d states between the K and K’ valleys that is responsible for the experimentally observed valley exciton splitting.

**S-terminated (111) polar surface.** For the S-terminated (111) polar surface, the Fermi energy falls into the valence band due to the polarity at the interface opposite to that in Eu-terminated surface. (A reconstructed non-polar surface, i.e., a surface with near equal number of S and Eu atoms, will have Fermi energy at the center of the bandgap.) There is still a small magnetic moment (~0.01 μB/f.u) observed in the TMD layer. It is worth to note that the band alignment between WS₂ and EuS is different from that between WS₂ and EuS due to difference in the bandgap of the two TMD systems. Bandgap of WS₂ is about 1.9 eV, while it is only ~1.3 eV for WSe₂. Because the bandgap of EuS of 1.6 eV is in between, in the conduction band, the W-d states of WS₂ appears to be inside the interface related bands (Fig. 5b). This is in clear contrast to Eu-terminated case, where W-d states are above the interface related S states (Fig. 5a). On the other hand, the W-d states of WSe₂ are located at the bottom of the conduction band and below the interface related states (Fig. 5d). As a result of this band alignment, larger exchange field is expected for WS₂ than for WSe₂ in the conduction band (see Table 3).

The valence band also show opposite shift of W-d states due to the presence of EuS compared to the one in case of Eu-terminated surface, similar to that of conduction band. Clearly, the magnitude of this exchange shift (~0.01–0.03 eV) is smaller both for WS₂ and WSe₂ than Eu-terminated case.

**W d-states energies at K and K’ valleys and valley A exciton splitting.** In the following discussions, we focus on excitonic transitions (A exciton) and valley exciton splitting. Unless otherwise specified, the conduction band and valence band refer to those of W d-states, and the band gap refers to the optical band gap. The energies of the lowest conduction and highest valence bands of TMDs are extracted and displayed in Table 2, to obtain the valley A exciton transition energies assuming vertical excitation at K and K’ points.

The exciton energies of TMDs depend on the relative shifts of valence and conduction bands due to the exchange interactions between the TMDs and the magnetic substrate, as shown in Table 2. The valley A exciton splitting, defined as ΔE = E(K) − E(K’), for WS₂ vs. WSe₂ on the nonpolar surfaces are quite different. For WS₂, it is relatively small and positive for Eu-terminated surface (+5.9 meV), while it is large and negative for S-terminated surface (~27.7 meV). The reconstructed nonpolar EuS surface is expected to have near equal ratio of S and Eu sites. Thus, averaging effects from Eu and S terminated surfaces should give reasonable expectation values of the net valley exciton splitting. Accordingly, the calculated valley A exciton splitting for WS₂ on EuS is about ~11 meV, which is not far from the experimental value of ~16 meV. For WSe₂ on EuS, on the other hand, the splitting is of similar value and positive for both Eu- and S-terminated surfaces. As a result, the averaged valley exciton splitting is about +9 meV. This is close to the value reported earlier by us considering the Eu-terminated polar surface alone. Thus, by considering the realistic EuS surface and competing exchange effects from the Eu- and S-terminated sites, our theoretical results are consistent with the experimentally observed sign reversal in valley exciton splitting in WS₂ compared to WSe₂.

**Fitting DFT results to the model Hamiltonian.** To fully understand the sign reversal in valley exciton splitting, we fitted the DFT results using minimum band model to extract the band gap, spin orbit coupling and exchange parameters. As discussed in our previous studies, the exchange field produces opposite band edge shifts at K and K’-valleys due to spin contributions, as the spin characters of the bands are opposite in different valleys. However, if exchange field would be the same for conduction and valence bands, then neither the spin (because interband optical excitation occurs between states of the same spin) nor the orbital moment would contribute to the exciton shift in a magnetic field due to reorientation of substrate magnetization. Thus, atomic orbital moment is expected to contribute to the valley exciton splitting in a manner similar to that from an external field. Nevertheless, the separation of the contributions of exchange effects from the spin and orbital moments is not straightforward. Therefore, we will discuss the combined effect as obtained in DFT + U calculations.

The Hamiltonian of TMDs, which has orbital parts, describing two band k·p gapped Dirac states with addition of spin–orbit coupling and exchange interactions are

\[
H_{\text{orb}} = \hbar v_f \left( \sigma_x k_x + k_y \sigma_y + k_z \sigma_z \right) + \frac{E_g}{2} \sigma_z,
\]

\[
H_{\text{SO}} = \tau_s \left[ \sigma_x + \tau_d \sigma_z \right],
\]

\[
H_{\text{exch}} = -s g \mu_B \left( B^r_x \sigma_x + B^r_y \sigma_y \right).
\]

Where \( v_f \) is the Fermi velocity of the Dirac electrons, \( E_g \) is the staggered potential (gap), \( \sigma_i \) are the pseudospin Pauli matrices operating on the sublattice A and B, \( \sigma_0 \) is the 2x2 matrix

\[
\begin{pmatrix}
0 & 1 \\
0 & 1
\end{pmatrix},
\]

\( \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \), \( \sigma_2 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \), \( \sigma_3 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \), and \( k_x \) and \( k_y \) are the Cartesian components of the electron wave vector measured from K(K); parameter \( \tau = 1 \) (−1) for K(K) valleys. \( \lambda_i \) and \( \lambda_i \) are intrinsic spin–orbit
parameters for the conduction and valence bands, respectively, and $s_z$ is the Pauli spin matrix in the $z$-direction. We have to introduce exchange fields $B^c_z$ and $B^v_z$ separately for the conduction and valence bands, to fit the obtained DFT eigenvalues because the DFT calculations reflect the combined effects and it is not straightforward to separate various contributions into a simple model.

The fitted band gaps ($\Delta$), the spin-orbit parameters for the conduction ($\lambda_c$) and valence ($\lambda_v$) bands, the band shifts due to the exchange ($\Delta E_{ex}^c$ and $\Delta E_{ex}^v$) and exciton valley splitting are shown in Table 3. Also shown are effective exchange fields ($B^c_z$ and $B^v_z$) in the parenthesis. Depending on terminations, the exchange interaction between the EuS substrate and W is mediated by either a single (in the case of Eu-termination) or double (in the case of S-termination) chalcogen sites. As can be seen from Table 3, the effective exchange fields for Eu-terminated surface sites are larger and positive (FM). The large on-site exchange field for the conduction and valence bands in TMDs is expected to be FM for a realistic EuS substrate with surface reconstruction. In the case of the A exciton, the effective exchange field always lowers (raises) the energy of spin up (down) bands in the $K$ ($K'$) valley (Fig. 7), and the valley splitting of the conduction and valence bands do not change sign for different TMD materials. The valley exciton splitting, on the other hand, is defined as the difference between the exciton transition energies of $K$ and $K'$ valleys. Its sign is dependent on the relative shift of the conduction and valence bands in the two valleys. For WS$_2$, the effective exchange field for the conduction band $B^c_z$ is smaller than that for the valence band $B^v_z$, i.e., the exchange splitting in the conduction band $\Delta E_{ex}^c$ is smaller than $\Delta E_{ex}^v$ in the valence band. The band gap in the $K$ valley $E_{g,K}^z$ thus increases while $E_{g,K}^{v'}$ decreases in the $K'$ valley, resulting in a negative valley exciton splitting $E_{ex}$ (see Fig. 7(a)). The situation for WSe$_2$ (Fig. 7(b)) is just the opposite, leading to a positive $E_{ex}$.

experimentally, magneto-reflectance were used to probe the valley exciton splitting. However, it cannot yield information on exchange splitting for the conduction and valence bands separately and thus the type of effective exchange interaction. Additional measurements by, for example, angle-resolved photoemission spectroscopy could give information about the occupied states, while inverse photoemission spectroscopy may shed light on the conduction states. Both experiments can be technologically relevant: while valley exciton splitting allows optical access of valley degree of freedom by light helicity and frequency, valley splitting of the conduction and valence bands allows electric gating to realize valley polarization of either electrons or holes.

From the above discussion, it can be seen that there are two essential factors in controlling the magnitude and sign of the valley exciton splitting in TMDs by magnetic proximity effect: the surface termination of EuS and the band alignment between TMDs and EuS. The indirect exchange interactions are FM for the one mediated by a single chalcogen bridge with Eu-termination, and AFM for the one mediated by a double chalcogen bridge with S-termination. This leads to competition between the two types of exchange interactions for a realistic EuS surface. Moreover, the band alignment determines the magnitude of the exchange splitting of the conduction and valence bands in TMDs.

### Discussion

One should clearly distinguish between the valley splitting of the conduction and valence bands, and the valley exciton splitting. The valley splitting of the conduction and valence bands is the energy difference of those bands between $K$ and $K'$ valleys, which depends on the effective exchange fields $B^c_z$ and $B^v_z$. For both WS$_2$ and WSe$_2$, the indirect exchange interactions are larger and FM for Eu-termination, while smaller and AFM for S-termination. As a result, the net effective exchange between TMDs and EuS is expected to be FM for a realistic EuS substrate with surface reconstruction. In the case of the A exciton, the effective exchange field always lowers (raises) the energy of spin up (down) bands in the $K$ ($K'$) valley (Fig. 7), and the valley splitting of the conduction and valence bands do not change sign for different TMD materials. The valley exciton splitting, on the other hand, is defined as the difference between the exciton transition energies of $K$ and $K'$ valleys. Its sign is dependent on the relative shift of the conduction and valence bands in the two valleys. For WS$_2$, the effective exchange field for the conduction band $B^c_z$ is smaller than that for the valence band $B^v_z$, i.e., the exchange splitting in the conduction band $\Delta E_{ex}^c$ is smaller than $\Delta E_{ex}^v$ in the valence band. The band gap in the $K$ valley $E_{g,K}^z$ thus increases while $E_{g,K}^{v'}$ decreases in the $K'$ valley, resulting in a negative valley exciton splitting $E_{ex}$ (see Fig. 7(a)). The situation for WSe$_2$ (Fig. 7(b)) is just the opposite, leading to a positive $E_{ex}$.

| Table 3 Parameters of the minimal band model calculated from the DFT band structure results |
|-----------------------------------------------|
| $\Delta$ (eV) | $\lambda_c$ (eV) | $\lambda_v$ (eV) | $E_{ex}^c(B^v_z)$ meV (T) | $E_{ex}^v(B^v_z)$ meV (T) | $E_{ex}(E_{ex}^c - E_{ex}^v)$ (meV) |
| WS$_2$, Eu-termination | 2.0368 | 0.0908 | 0.3768 | 27.7 (478) | 24.8 (428) | +5.8 |
| WS$_2$, S-termination | 1.9063 | 0.0184 | 0.3831 | −18.1 (−311) | −4.3 (−74) | −27.6 |
| WSe$_2$, Eu-termination | 1.6442 | 0.0297 | 0.3921 | 45.0 (777) | 41.0 (708) | +8 |
| WSe$_2$, S-termination | 1.6442 | 0.0297 | 0.3921 | −8.6 (−149) | −13.5 (−233) | +9.8 |
Together, they can determine the sign of valley exciton splitting depending on whether the band gap is widened or narrowed in K and K’ valleys. Such understanding provides important guidance for designing the TMD/Magnetic heterostructures with tunable valley splitting. For example, surface termination can be varied by controlling the growth orientation of single crystalline EuS using molecular epitaxy; band alignment can be tuned by different combinations of magnetic materials and TMDs; and alloying of different TMDs such as W(S,Se)2 can lead to continuous tuning of the magnitude and sign of valley exciton splitting. Giant enhancement in valley exciton splitting, together with tunable magnitude and sign, would allow versatile control of valley pseudospin, enabling its arbitrary rotation and switching, and possibly entangled pseudospins with controllable phases. Most recently, several groups reported discovery of intrinsic 2D ferromagnetic materials. Combining these 2D magnets with 2D TMDs may offer a practical approach for emerging valleytronics applications.

Magnetic proximity effect from a ferromagnetic EuS substrate results in a giant valley exciton splitting in monolayer WS2. A sign reversal from positive for WSe2 to negative for WS2 is also observed. This is attributed to the competing exchange interactions for Eu- and S-termination for a realistic EuS substrate with surface reconstruction, together with different band alignments between TMDs and EuS. The ability to tune the magnitude and sign of valley splitting allows convenient control of valley pseudospin for quantum information processing.

### Methods

#### Sample preparation

Monolayer TMDs, including WSe2 and WS2, were prepared by selenization or sulfurization of electron-beam evaporated ultrathin transition-metal-oxide films on substrate substrates. Details are in supporting information.

#### Film transfer

The as-grown monolayer TMD films were transferred onto Si/SiO2 and EuS substrates by modified published procedures. Briefly, monolayer WSe2 or WS2 on a sapphire substrate was spin-coated by polystyrene (PS). After 5 min baking at 120 °C, a water droplet was placed on the PS surface. The sample’s edge was then poked by tweezers, and the water penetrated between the film and the substrate. After several minutes, the film completely separated from the substrate and floated on the water surface. The film was then transferred onto a Si/SiO2 or EuS substrate, followed by 5 min baking at 80 °C. The baking of PS at sufficiently high temperatures will eliminate wrinkles in the TMDs. The PS was removed by immersing the sample in toluene for 15 min. After repeated cleaning, the sample was then annealed in an ultrahigh vacuum chamber at 350 °C for 180 min to remove any PS residual and improve the interface quality.

### Optical measurements

For magneto-reflectance measurements, the samples were placed on the cold finger of a continuous-flow optical cryostat operated in the 5–300 K temperature range. The cryostat was mounted on a three-axis translator with a spatial resolution of 10 μm in each direction. The x- and y-translations stages allow us to access a single TMD crystal. The cryostat tail was positioned inside the room temperature bore of a 7 T superconducting magnet. A collimated white light beam was used for the reflectivity work. The incident light was focused on the sample using a microscope objective with a working distance of 34 mm. The incident beam was polarized either as σ+ or σ− using a Babinet–Soleil compensator. The objective collected the reflected beam from the sample in the Faraday geometry and the light was focused onto the entrance slit of a single monochromator that uses a cooled charge-coupled device detector array.

### Magnetization measurements

The field-dependent magnetization of EuS at different temperatures was measured by the VSM option of a quantum design physical property measurement system. The magnetic field was applied in the direction perpendicular to the film plane, and thus only the out-of-plane component of the magnetic moment was measured.

### Computational details

Density functional-based calculations are performed by using the projector augmented wave method (as implemented in VASP) within GGA-PBE approximations. van der Waals interaction is taken into consideration using the DFT-D3 method. Electron wave function cut off energy is 400 eV. The vacuum of about 15 Å separates periodically repeated slabs. Structural relaxation is carried out using the conjugate-gradient algorithm until the Hellmann–Feynman force on each atom is less than 0.01 eV/Å. For magneto-reorientation work, the incident light was focused on the sample using a microscope objective with a working distance of 34 mm. The incident beam was used for the reflectivity work. The incident light was focused on the sample using a microscope objective with a working distance of 34 mm. The incident beam was polarized either as σ+ or σ− using a Babinet–Soleil compensator. The objective collected the reflected beam from the sample in the Faraday geometry and the light was focused onto the entrance slit of a single monochromator that uses a cooled charge-coupled device detector array.

### Data availability

All data supporting the findings in this manuscript are available from the corresponding authors (A.P., R.S. and H.Z.) upon request.

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Author contributions

H.Z. and A.P. conceived, designed, and guided the experiments. T.N., C.Z. and P.Z. performed the experiments and data analysis. R.S. performed the first-principle calculations. H.Z. and R.S. wrote the paper. All the authors commented on the paper.

Additional information

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