Contrast in spin-valley polarization due to competing indirect transitions in few-layer WS$_2$ and WSe$_2$

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Controlling the momentum of carriers in semiconductors, known as valley polarization, is a new resource for optoelectronics and information technologies. Materials exhibiting high polarization are needed for valley-based devices. Few-layer WS$_2$ shows a remarkable spin-valley polarization above 90%, even at room temperature. In stark contrast, polarization is absent for few-layer WSe$_2$ despite the expected material similarities. Here, we explain the origin of valley polarization in both materials due to the interplay between two indirect optical transitions. We show that the relative energy minima at the $\Lambda$- and K-valleys in the conduction band determine the spin-valley polarization of the K-K transition. Polarization appears as the energy of the K-valley rises above the $\Lambda$-valley as a function of temperature and number of layers. Our results advance the understanding of the high spin-valley polarization in WS$_2$. This insight will impact the design of both passive and tunable valleytronic devices operating at room temperature.
Keywords: few-layer transition metal dichalcogenides; valleytronics; WS$_2$; WSe$_2$; indirect transitions; interlayer interaction.

Transition metal dichalcogenides (TMDs) such as MoS$_2$, WS$_2$, or WSe$_2$ are layered semiconductors with unique spin-valley physics. The coupling between spin and momentum for excited carriers opens a new path to access the valley degree of freedom$^1$. Valley polarization arises from a difference in exciton populations at the K- and K’-points of the hexagonal Brillouin zone (Figure 1a)$^{1-3}$, where local energy minima (valleys) lie. At these diametrically opposite points, spin-orbit splitting in the valence band occurs with different signs$^4$, resulting in the coupling of spin and valley indexes and leading to spin-dependent optical and electronic properties. The K- and K’-valleys can be selectively excited using right- or left-handed circularly polarized light$^5$. TMDs thus constitute a fascinating platform for future valleytronic$^6$, optoelectronic$^7$–$^9$, and nanophotonic$^{10,11}$ devices exploiting spin, valley, and layer indexes.

The layered nature of TMDs enables a high degree of control over valley polarization. A monolayer possesses a direct band gap, whereas in the few-layer regime the band gap becomes indirect$^{12-14}$. Light emission in few-layer TMDs is dominated by indirect transitions from the Λ- and K-points to the Γ-point in the band structure (Figure 1a). These indirect transitions are typically unpolarized. Higher in energy, polarized transitions can still occur in the K- or K’-valleys. The degree of circular polarization is a proxy for valley polarization defined as DOCP = ($I_{\sigma+} - I_{\sigma-}$)/($I_{\sigma+} + I_{\sigma-}$), where $I_{\sigma+}$ and $I_{\sigma-}$ are the photoluminescence intensities with right- and left-handed circular polarization, respectively. Valley polarization can reach values near unity at cryogenic temperatures for monolayer MoS$_2$ on insulating substrates$^1$. With increasing temperature, however, the initial polarization quickly depolarizes due to inter-valley scattering.
between the K- and K'-points\textsuperscript{15}, limiting applications at room temperature. At higher temperatures, a valley polarization enhancement for a monolayer has been realized through interaction with graphene\textsuperscript{16,17}, reaching up to 40\% DOCP for graphene-encapsulated WS\textsubscript{2}\textsuperscript{18}. In contrast to monolayers, for bilayer WS\textsubscript{2} the DOCP reaches 65\% on insulating substrates even at room temperature\textsuperscript{19}. Such a large spin-valley polarization in bilayer WS\textsubscript{2} is not well-understood yet\textsuperscript{20,21}.

Despite sharing several properties with WS\textsubscript{2} due to the common W atom, valley polarization is absent in WSe\textsubscript{2} at room temperature. This discrepancy between bilayer WS\textsubscript{2} and WSe\textsubscript{2} (Figure 1c and 1d) remains unresolved, as stated by Bussolotti \textit{et al}\textsuperscript{20}. An understanding of the spin-valley properties leading to high and low polarization in WS\textsubscript{2} and WSe\textsubscript{2} is, therefore, essential for practical applications at room temperature\textsuperscript{22}. Additional insight into the spin-valley physics of bilayer TMDs would also be beneficial for spin-layer locking effects\textsuperscript{23–26}, layer-dependent spin relaxation\textsuperscript{27}, and the spin-valley Hall effect in few-layer systems\textsuperscript{28,29}.

Here, we demonstrate the critical role of the Λ-valley on the spin-valley polarization in few-layer WS\textsubscript{2} and WSe\textsubscript{2} through a combined investigation of polarization- and temperature-resolved photoluminescence (PL). By varying both the number of layers and the temperature, we analyze the interplay between the momentum-allowed direct transition (K-K) and two momentum-forbidden indirect transitions (K-Γ and Λ-Γ). We find that as the dominant indirect transition channel changes as a function of temperature, it determines the spin-valley polarization. In bilayer WSe\textsubscript{2}, we reveal the existence of a crossover temperature at which the dominant indirect transition switches from K-Γ to Λ-Γ as the Λ-point energy shifts lower in energy than the K-point. Below this crossover temperature, the polarization of the direct K-K transition begins to increase. We demonstrate the dependence of the K-K valley polarization on the conduction band K-Λ energy.
difference. In contrast to WSe$_2$, in WS$_2$ the $\Lambda$-$\Gamma$ indirect transition dominates the emission even at room temperature resulting in high polarization. Based on our results, we explain how both temperature and number of layers affect spin-valley polarization in WS$_2$ and WSe$_2$, identifying a missing piece of the puzzle for understanding and achieving high spin-valley polarization in few-layer semiconductors.

**Figure 1** | Direct and indirect optical transitions in few-layer TMDs and their spin-valley polarizations. a, Schematic of the exciton transitions leading to different photoluminescence peaks. Two indirect transitions are possible depending on the conduction band minimum involved being either at the K- or the $\Lambda$-valley. Their relative energy difference is $\Delta E_{K-\Lambda}$. The K-K’ inter-valley scattering is omitted for clarity. b, Illustration of a bilayer WS$_2$ or WSe$_2$ and the orbital characters of the K- and $\Lambda$-valleys. The interlayer interactions through the $p$-orbitals control the
Λ-point energy resulting in changes of $\Delta E_{K-\Lambda}$. b, Polarization-resolved photoluminescence spectra for bilayer WS$_2$ and d, bilayer WSe$_2$ at room temperature show high polarization in WS$_2$ and no polarization in WSe$_2$.

**Spin-valley polarization in few-layer WS$_2$ and WSe$_2$**

First, we consider the typical band structure of a bilayer TMD (Figure 1a). In contrast to the monolayer case, the bilayer band gap is indirect because the valence band maximum shifts from K to $\Gamma$ from one to two layers. The nature of the indirect transition depends on the competition between the $\Lambda$ and K conduction band energy minima (orange and light green arrows in Figure 1a). To study these indirect transitions, we exploit temperature and number of layers as tuning knobs for the band structure.

The effect of interlayer interactions on the band structure is highly dependent on momentum, leading to a different layer and temperature dependence for the energy of the K-K, K-$\Gamma$, and $\Lambda$-$\Gamma$ transitions (Table 1)$^{15,30}$. At the K-point, $d$-orbitals from the transition metals determine the topmost band structure$^5$. Increasing the temperature expands the covalent bond length between the atoms reducing the energy gap at the K-point. The transition metal atoms lie protected between the chalcogens, which results in insensitivity of the K-point to the surrounding medium and, therefore, to the number of layers. On the other hand, the chalcogen atoms lie close to both the surrounding medium and adjacent layers. The chalcogen $p$-orbitals that dominate at the $\Lambda$-point extend outside the atomic plane, rendering it sensitive to interlayer interactions (Figures 1b)$^{30}$. With increasing temperature, the out-of-plane $p$-orbitals extend in length and come closer to each other, thereby increasing their interaction because the interlayer distance due to van der Waals forces between the layers is not temperature dependent. Consequently, the $\Lambda$-valley increases in energy with increasing temperature. Increasing the number of layers, on the contrary, results in a
decrease of the Λ-valley energy because more out-of-plane $p$-orbitals interact with neighboring layers. As summarized in Table 1, we can utilize both temperature and the number of layers to vary the direct and indirect transitions of WS$_2$ and WSe$_2$.

Table 1 | Both the temperature and the number of layers affect the band structure of few-layer WS$_2$ and WSe$_2$, with different dependences of the transition energies between different points in momentum space.

| Energy   | Increase #L | Increase $T$ |
|----------|-------------|--------------|
| $E_{K-K}$ | Near constant | Decreases    |
| $E_{\Lambda-\Gamma}$ | Decreases | Increases    |
| $E_{K-\Gamma}$ | Decreases | Decreases    |

To compare the valley polarization of WS$_2$ and WSe$_2$, we excite our samples with circularly polarized light and measure the polarization of the emission with a circular polarization analyzer and a spectrometer (see Methods). We observe a stark difference in circular polarization for bilayer WS$_2$ and WSe$_2$ (compare high and low values in Figures 1c and 1d). To clarify the origin of these contrasting polarizations, we measure next the changes in spectra and polarization as a function of the number of layers and temperature.

The role of the indirect optical transitions in polarization

We prepare samples with varying numbers of layers of WS$_2$ and WSe$_2$ (see Methods). We measure their PL spectra and determine the position of the direct and indirect transition peaks (Supporting Figures 1 and 2). The peak energies as a function of the number of layers show that the separation between the direct and indirect peaks increases faster with thickness for WS$_2$ compared to WSe$_2$ (Figures 2a and 2b). This difference is a consequence of the origin of their indirect emission, which stems from Λ-Γ transitions in WS$_2$ while it originates from K-Γ transitions in WSe$_2$ at room
temperature. The larger increase in energy shift with thickness for the Λ-Γ transition is due to the larger impact of interlayer interactions on the Λ-valley compared to the K-valley.

Figure 2 | The spin-valley polarization of WS₂ and WSe₂ have different dependences on the number of layers at room temperature. a-b, Photoluminescence peak positions of the transitions. c-d, Circular polarization of the K-K band maximum for different numbers of layers of WS₂ and WSe₂, respectively. We retrieve the polarization of the K-K transition from Gaussian fitting of all the spectra with both circular polarizations in order to remove any possible spectral overlap with an indirect transition. The dashed lines are guides to the eye.

Next, we measure how polarization changes for a varying number of layers (Figures 2c and 2d). For WS₂, the polarization of K-K emission quickly increases from mono- to trilayer, reaching DOCP = 0.89 and saturating for thicker samples. For WSe₂, the polarization of the K-K emission
remains absent for all thicknesses. As expected, the K-Γ and Λ-Γ transitions are unpolarized in all measurements (Supporting Figures 2 and 3). We deconvolute the polarization contribution of each transition by fitting the spectra with Gaussian functions (see Methods). Thanks to this fitting, we remove any contribution from the unpolarized indirect PL emission in our polarization analysis to retrieve the DOCP for the PL maximum of the peak.

The insensitivity of the polarization to thickness in WSe₂ is in clear contrast to the dependence in WS₂. As the main change in band structure with increasing thickness is a decrease in energy of the Λ-Γ transition, $E_{\Lambda-\Gamma}$, we can reasonably expect that an increasing difference between $E_{K-K}$ and $E_{\Lambda-\Gamma}$ could control the increase in circular polarization in WS₂. To validate this hypothesis, however, we need to determine the conditions required for increasing the DOCP in WSe₂. Changing the temperature is a controllable way to perturb the band structure in both materials. Thus, we measure next the PL spectra and DOCP at lower temperatures and track the PL peak position (Figure 3 and Supporting Figure 4). In bilayer WS₂, the direct and indirect exciton peaks move to higher and lower energies with decreasing temperature, respectively (Figure 3a). In WSe₂, the situation is different. First, the K-Γ peak shifts to higher energy with decreasing temperature because the K-point is the conduction band minimum in this temperature range\textsuperscript{30}. Below 160 K, the indirect peak starts moving to lower energies with decreasing temperature (Figure 3b), which is consistent with the indirect peak now arising from Λ-Γ transitions.

We describe the evolution of the peak energies with temperature (Figure 3a and b) using the Varshni equation\textsuperscript{31}

$$E_g(T) = E_g(0) - \frac{aT^2}{\beta + T}$$

(1)
Figure 3 | Relation between the indirect band gap character and spin-valley polarization. The polarization of the K-K transition in WSe$_2$ starts increasing when the band gap minimum shifts from K-$\Gamma$ to $\Lambda$-$\Gamma$. a-b, Temperature dependence of the photoluminescence peak position for direct and indirect transitions. c-d, Temperature dependence of the circular polarization of the K-K transition maximum for bilayer WS$_2$ and WSe$_2$, respectively. The solid lines are fittings described in the text.

where $T$ is the temperature, $E_g(0)$ is the excitonic band gap at $T = 0$ K, and $\alpha$ and $\beta$ are phenomenological fitting parameters. For the indirect exciton in WSe$_2$, we use two separate Varshni equations for the high- and low-temperature regimes due to the change in indirect transition character at $T = 160$ K. We list the fitting parameters in Table 2. The parameter $\alpha$ describes the band gap change with temperature due to thermal expansion of the lattice. The values of $\alpha = 0.53$ meV/K for the K-K transition and $\alpha = -0.172$ meV/K for the $\Lambda$-$\Gamma$ transition are equal
for both WS$_2$ and WSe$_2$. This similarity is evidence of similar band structure changes with temperature for both materials. However, since bilayer WSe$_2$ has a smaller band gap than WS$_2$, the K-K, and Λ-Γ gaps will be closer in energy in WSe$_2$. Therefore, the crossover of the indirect transitions occurs at a lower temperature in WSe$_2$ than in WS$_2$.

**Table 2** Fitting parameters using the Varshni equation for the temperature dependence of emission the different transitions and materials in Figures 3a and 3b.

| Material / Transition | $E_g(0)$ (eV) | $\alpha$ (meV/K) | $\beta$ (K) |
|-----------------------|----------------|-----------------|-------------|
| **WS$_2$**            |                |                 |             |
| K-K                   | 2.045          | 0.530           | 118.9       |
| Λ-Γ                   | 1.737          | -0.172          | 12.5        |
| **WSe$_2$**           |                |                 |             |
| K-K                   | 1.713          | 0.530           | 139.3       |
| K-Γ                   | 1.600          | 0.316           | 96.6        |
| Λ-Γ                   | 1.546          | -0.172          | 44.1        |

The measured polarization rises with increasing thickness in WS$_2$ because it corresponds to a higher K-Λ energy separation of the conduction bands. Similarly, this energy separation also increases with decreasing temperature. Indeed, for bilayer WS$_2$ the circular polarization increases with decreasing temperature (Figure 3c). At temperatures from 300 to 160 K, valley polarization remains absent in WSe$_2$. In this range, the $E_{K-K}$-$E_{K-Γ}$ separation does not vary substantially because both peaks shift to higher energy with decreasing temperature (gray points in Figure 3d). As the temperature reduces below $T = 160$ K, the indirect transition changes from K-Γ to Λ-Γ. Simultaneously, the polarization of the K-K transition starts to increase and saturates at low temperatures (Figure 3d). At these low temperatures, bilayer WSe$_2$ behaves like bilayer WS$_2$ because their indirect transitions have now both Λ-Γ character, as evidenced by their similar Varshni dependences. Our polarization values at low temperature (T~10 K) are consistent with previous measurements using similar excitation energies for both materials$^{19,32}$. Our results show
the critical role of the Λ-valley in establishing spin-valley polarization due to the dependence of
the polarization of the K-K transition on the origin of the indirect transition.

To compare the temperature dependence of polarization in both materials, we fit the DOCP as
a function of temperature (Figures 3c and 3d) using the expression

$$DOCP = \frac{P_0}{1 + \frac{\tau_B}{\tau_v}}$$

(2)

which takes into account the K-K exciton transition rate ($1/\tau_B$) and K-K’ intervalley scattering rate
($1/\tau_v$). $P_0$ is the initial polarization before scattering takes place, for which we use the maximum
DOCP at the lowest measured temperature. We assume a Boltzmann distribution for the ratio
$\tau_B/\tau_v = c \exp(-\Delta E/k_B T)$, where $c$ is a constant and $\Delta E$ is an activation energy (see Supporting
Table 1 for fitting parameters).

Next, we explicitly demonstrate that the polarization of the direct K-K transition in WSe$_2$
depends on the conduction band K-Λ energy difference, $\Delta E_{K-Λ}$. First, we calculate $\Delta E_{K-Λ}$ as a
function of temperature from the fittings in Figure 3b as $\Delta E_{K-Λ} = E_{K-Γ} - E_{Λ-Γ}$ (Figure 4a). The
polarization of the K-K emission starts increasing when $\Delta E_{K-Λ}$ becomes positive (Figure 4b).

Previously, the Γ-hill has been suggested to block K-K’ inter-valley scattering of holes in bilayer
WS$_2^{33}$. That hypothesis is not consistent, however, with the absence of valley polarization in WSe$_2$
at higher temperatures, where the dominant indirect transition is Λ-Γ. A comparison of $\Delta E_{K-Λ}$ in
the conduction band and $\Delta E_{Γ-K}$ in the valence band ($\Delta E_{Γ-K} = E_{K-K} - E_{K-Γ}$) further supports the
relevance of the Λ-valley on polarization (Figure 4a). The energy difference in the valence band
$\Delta E_{Γ-K}$ is already far above the thermal energy at room temperature, so its weak increase with
decreasing temperature cannot influence polarization substantially. On the other hand, $\Delta E_{K-Λ}$
varies in a lower energy range and will be more affected by the thermal energy, consistent with the temperature dependence of the K-K polarization (Figure 3d) and its appearance after $\Delta E_{\Gamma-K}$ becomes positive (Figure 4b). Our results thus prove the important role of the $\Lambda$-valley in protecting spin-valley polarization in few-layer semiconductors.

**Figure 4** The polarization of the direct K-K emission in WSe$_2$ depends on the energy difference between the conduction band points of the indirect transitions. a, Temperature dependence of the $\Delta E_{K-\Lambda}$ of the conduction band and the $\Delta E_{\Gamma-K}$ of the valence band obtained from the three fittings in Figure 3b. b, Polarization of the K-K photoluminescence as a function of the $\Delta E_{K-\Lambda}$ conduction band change. Inset: schematic of the band diagram responsible for the changes in K-K polarization determined by the value of $\Delta E_{K-\Lambda}$.

**Mechanisms for spin-valley polarization in few-layer semiconductors**

To better illustrate the appearance of polarization below the indirect transition crossover temperature (Figures 3b and 3d), we consider the following scheme for bilayer WSe$_2$. When $T > 160$ K, the indirect transition is K-$\Gamma$ and polarization is absent for the K-K transition (Figure 5, left). In W-based TMDs, the transition between the lowest conduction band and the top valence band at K is spin-forbidden (dark K-K exciton) due to spin splitting. Because there is no inter-
valley exchange interaction for the dark exciton states\textsuperscript{15}, they can act as an exciton reservoir for bright K-K valley polarization\textsuperscript{34}. However, as the Γ-hill has no spin splitting, the K-Γ transition depopulates the dark exciton reservoir contributing to depolarization. As the temperature decreases, Λ moves to an energy similar to K. There is an intermediate temperature range where both K-Γ and Λ-Γ transitions contribute to the indirect exciton emission and the K-K polarization starts to increase (Figure 5, middle). The overlap in emission from both indirect transitions is evident from the fitting of the indirect spectral band, where two Gaussians are necessary. Finally, as ΔE\textsubscript{K-Λ} increases, only the Λ-valley contributes to indirect emission resulting in a faster increase of polarization with decreasing temperature (Figure 5, right). In this temperature range, the K-K dark exciton reservoir is restored due to the spin splitting at Λ\textsuperscript{20,35}, resulting in higher polarization. Additionally, phonons affect polarization\textsuperscript{21} and we also expect a significant difference in phonon coupling for K-Γ and Λ-Γ transitions.

To quantify the bright-dark exciton splitting, we investigate the total K-K PL intensity as a function of temperature (Supporting Figure 5). We observe a decrease of K-K intensity with decreasing temperature, which is a typical trend of reduced thermalization of excitons from dark to bright states\textsuperscript{36,37}. We fit the measured integrated PL intensity as a function of temperature to the expression $I\text{PL}(T)/I\text{PL}(0) - 1 = C \exp(-E_D/k_B T)$, where $I\text{PL}(T)$ is the measured intensity as a function of temperature, $I\text{PL}(0)$ is the intensity at $T = 0$ K, $C$ is a constant, $k_B$ is the Boltzmann constant, and $E_D$ is the characteristic energy barrier that defines the slope of the emission. From the fit, we obtain $E_D = 37.9$ meV, which is in good agreement with the bright-dark exciton splitting in monolayer WSe\textsubscript{2}\textsuperscript{38}. We expect a similar value for bilayer WSe\textsubscript{2} due to the limited effect of layer-layer interactions on the band structure near the K-point of the Brillouin zone. The bright-dark splitting in monolayer WS\textsubscript{2} is $\sim 55$ meV\textsuperscript{38}. Due to this higher value, the effect of the dark states for
stabilizing a more robust valley polarization should be stronger at elevated temperatures in WS\textsubscript{2} compared to WSe\textsubscript{2} in agreement with our observations. Similarly to WSe\textsubscript{2}, we expect the polarization in WS\textsubscript{2} to vanish when $\Delta E_{K-\Lambda}$ becomes negative at a higher temperature.

**Figure 5** | Effect of the K-\Lambda crossover on the K-K spin-valley polarization. a, Photoluminescence spectra and b, band structure schematics illustrate the conditions leading to the appearance of polarization in WSe\textsubscript{2} at three different temperatures. The emission spectra include fittings to a Gaussian function for the detected $\sigma_+$-polarization spectra. At $T = 170$ K (left column), there is no polarization and the $\Lambda$-valley is not yet involved in the transitions. At this temperature, the K-$\Gamma$ transition can deplete the spin-down K-valley because there is no spin splitting in the $\Gamma$-hill. At $T = 120$ K (center), a small spin-valley polarization appears as the $\Lambda$-valley now takes part in the optical transitions. Here, two Gaussians are necessary for fitting the indirect photoluminescence peak. At $T = 30$ K (right), only the $\Lambda$-valley contributes to the indirect emission resulting in higher polarization. Due to spin splitting in the $\Lambda$-valley, the spin-down K-valley is no longer depleted through indirect optical transitions and becomes dark.
The dependence of polarization on the number of layers is also in agreement with the mechanism in Figure 5. For WS₂, there is a significant difference in polarization between bilayers (DOCP ≈ 0.65) and trilayers (≈ 0.95) at room temperature (Figure 2c). The additional layer shifts the Λ-valley to lower energy, while the K-valley remains nearly constant (Figure 2a). To confirm this behavior in WSe₂ as well, we perform temperature- and polarization-resolved PL measurements on tri- and four-layer WSe₂ (Supporting Figure 6). The polarization starts to increase at a higher temperature than in bilayer WSe₂ as the number of layers increases. The results are consistent with the expectation of a smaller ΔE_{K-Λ} energy separation at elevated temperatures.

**Conclusion**

In summary, we have demonstrated the impact of the Λ-valley on spin-valley polarization in WS₂ and WSe₂ through temperature- and polarization-resolved photoluminescence measurements. By varying the temperature and the number of layers, the position of the conduction band Λ-valley changes relative to the K-valley. We show that the conduction band Λ-K energy difference controls the K-K spin-valley polarization. In bilayer WSe₂, we correlate the appearance of polarization with the crossover between indirect transitions below \( T = 160 \text{ K} \), when the Λ-valley becomes the conduction band minimum. The polarization increases with increasing energy difference between the K- and Λ-valleys. This observation highlights the importance of the Λ-valley in blocking K-K’ inter-valley scattering to stabilize polarization.

Our results introduce the critical role of indirect optical transitions in spin-valley polarization in few-layer semiconductors. In particular, they contribute to the understanding of the exceptionally high spin-valley polarization in few-layer WS₂. For WS₂, the energy of the Λ-valley is already below the K-valley at room temperature. Polarization increases with the number of
layers in WS$_2$ because of the higher K-$\Lambda$ energy difference. The \( \Lambda \)-valley thus determines the contrast between the high polarization in few-layer WS$_2$ and low polarization for monolayer WS$_2$ and few-layer WSe$_2$ at room temperature, for which the \( \Lambda \)-valley does not intervene. Such a protection of polarization by the emergence of an indirect transition is a striking manifestation of interlayer interactions at the sub-nanometer scale. The control of the band structure and its indirect transitions by changing the interlayer distance (\textit{e.g.}, using strain or pressure), tuning the band gap (\textit{e.g.}, via electrical gating), or through hetero- or homostructures opens a route to manipulate the entanglement of the spin, valley, and layer indexes for actively tunable valleytronics.

**Methods**

**Sample fabrication.** We deposit WS$_2$ and WSe$_2$ flakes onto SiO$_2$/Si (85-nm thick SiO$_2$) substrates by mechanical exfoliation from synthetic, bulk 2H crystals (HQ Graphene). We first determine the thickness of the flakes by optical contrast microscopy and by considering the energy of the indirect exciton emission in photoluminescence spectra. Following critical measurements, we confirmed the thickness by atomic force microscopy.

**Optical measurements.** We carry out photoluminescence measurements using a microscope in epi-fluorescence geometry with a low numerical-aperture objective lens (Nikon CFI Plan Fluor ELWD 40x, NA = 0.6). We excite with a continuous-wave laser with photon energy 2.040 eV and a power of 12.2 \( \mu \)W before the objective lens, ensuring a power density in the linear response range for the TMDs. To control the circular polarization in excitation, we employ a Babinet-Soleil compensator and a Stokes polarimeter (PolSNAP, Hinds Instruments) at the sample position to ensure circular polarization of the incident laser beam. In the detection path, we use a non-polarizing beamsplitter (21014 Silver Non-Polarizing 50/50 bs Chroma), two 615 nm longpass
filters (ET615LP Chroma), and a polarization analyzer consisting of a quarter-wave plate (Bernhard Halle achromatic quarter-wave retarder, 600-1200 nm) and a wire-grid polarizer (Thorlabs WP25M-UB). After coupling into an optical fiber with core size 50 µm, we record PL spectra with an Andor Shamrock 303 spectrometer and an Andor Newton EMCCD camera. For low-temperature measurements, we use a liquid helium flow cryostat (Oxford Instruments MicrostatHiRes) pumped to ultra-high vacuum.

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