Supplementary Information

Impact of indirect transitions on valley polarization in WS$_2$ and WSe$_2$

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Supplementary Section S1: Room temperature photoluminescence

1. Resonant excitation of bilayer WSe$_2$
Throughout our study, we report polarization values measured with excitation at a constant photon energy of 2.040 eV, which is close to resonance for bilayer WSe$_2$. Here, we check that bilayer WSe$_2$ does not show spin-valley polarization either under resonant excitation conditions (Supplementary Figure S1). We used an excitation energy of 1.681 eV, which is close to the WSe$_2$ bilayer K-K exciton emission around 1.62 eV.

![Supplementary Figure S1](image.png)

Supplementary Figure S1. a, Polarization-resolved PL spectrum for bilayer WSe$_2$ under near-resonant excitation (1.681 eV) at room temperature. b, Degree of circular polarization as a function of photon energy. No DOCP is measurable.

2. Thickness-dependent polarization
We determine the thickness of our WS$_2$ and WSe$_2$ samples by using a combination of reflection contrast microscopy, atomic force microscopy, and photoluminescence measurements. Similarly, for both WS$_2$ and WSe$_2$, the monolayers show bright emission due to their direct band gap. At room temperature, their emission spectrum shows a single peak. When increasing the thickness, a second peak emerges, which shifts to lower energy with an increasing layer thickness.
(Supplementary Figure S2). Only WS\textsubscript{2} shows an increase in the DOCP with thickness, whereas in WSe\textsubscript{2} the emission remains unpolarized for all thicknesses when excited with 2.04 eV (Supplementary Figure S3) and 1.796 eV (Supplementary Figure S4).

Supplementary Figure S2. Polarization-resolved PL spectra at room temperature for different thicknesses. a, WS\textsubscript{2}. b, WSe\textsubscript{2}. Spectra are vertically shifted by a constant for clarity.
Supplementary Figure S3. Degree of circular polarization at room temperature as a function of emission wavelength for a set of different thicknesses for a, WS$_2$, and b, WSe$_2$. 
Supplementary Figure S4. Polarization-resolved PL spectra at room temperature for different thicknesses of WSe$_2$ excited with 1.796 eV. **a**, Thickness dependent spectra. **b**, Thickness vs the DOCP and the direct-indirect energy difference for the spectra in **a**.
Supplementary Section S2: Temperature-dependent photoluminescence

1. Bilayer photoluminescence spectra

When the temperature decreases, the two photoluminescence peaks shift with temperature (Supplementary Figure S4). In bilayer WS$_2$, the polarization also increases. However, in bilayer WSe$_2$, polarization only appears below $T = 160$ K (Supplementary Figure S5).

**Supplementary Figure S5.** Polarization-resolved PL spectra at different temperatures for bilayer samples. **a,** WS$_2$. **b,** WSe$_2$. Spectra are vertically shifted by a constant for clarity.
Supplementary Table S1. Fitting parameters obtained using Equation 2 in the main text in Figure 3. We contained the factor of 2 in the denominator of Equation 2 in the fitting parameter, $c$.

| Material | $c$  | $\Delta E$ (meV) |
|----------|------|------------------|
| WS\(_2\) | 0.12 | 74.6             |
| WSe\(_2\) | 0.076 | 72.5             |

2. Fitting using the O'Donnell equation

We fit the peak position as a function of temperature using two equations. Fitting using the Varshni equation\(^1\) was presented in the main text. Here, we fit the peak position using the O’Donnell equation\(^1\)

$$E_g(T) = E_g(0) - S\langle \hbar \omega \rangle \left[ \coth \left( \frac{\langle \hbar \omega \rangle}{2k_B T} \right) - 1 \right]$$  \hspace{1cm} (S1)

where $T$ is the temperature, $E_g(0)$ is the excitonic band gap, $S$ is the Huang-Rhys factor, $\langle \hbar \omega \rangle$, is an average phonon energy, and $k_B$ is the Boltzmann constant. The obtained fitting parameters are listed in Supplementary Table S2. Fitting using the O’Donnell equation yields as good a fit as with the Varshni equation, i.e., $R^2 = 0.9999$ when comparing the two fits. The main variation one might encounter between these two fitting methods will be expressed mainly in the range $T=0-20$ K, where we do not have several data points, as the band gap energy varies less in this range. The O’Donnell equation has a more profound theoretical background, and its fitting parameters are more well defined\(^1\). The Huang-Rhys factor, $S$, describes the exciton-phonon coupling strength of a certain transition. Comparing the values for each transition in Supplementary Table S2, we note that the exciton-phonon coupling strength is much larger for transitions that involve electrons in the K-valley compared to the $\Lambda$-valley. Similarly, the average phonon energy is also smaller for $\Lambda$-$\Gamma$ excitons, suggesting that $\Lambda$-$\Gamma$ excitons are more resistant to scattering by phonons.
Supplementary Table S2. Fitting parameters obtained using Equation S1 with the experimental data in Figure 3a-b.

| Material / Transition | $E_g(0)$ (eV) | $S$ (°) | $\langle h\omega \rangle$ (meV) |
|-----------------------|--------------|--------|-------------------------------|
| WS$_2$               |              |        |                               |
| K-K                  | 2.045        | 2.979  | 14.6                          |
| Λ-Γ                  | 1.737        | 0.997  | 2.0                           |
| WSe$_2$              |              |        |                               |
| K-K                  | 1.713        | 2.957  | 16.5                          |
| Κ-Γ                  | 1.600        | 1.791  | 12.4                          |
| Λ-Γ                  | 1.546        | 0.991  | 6.3                           |

3. Evidence of a dark ground state in bilayer WSe$_2$

In W-based monolayers, the dark excitons lie lower in energy than the bright excitons and transitions between the lowest conduction band and the top valence band at K is spin-forbidden (dark K-K exciton) due to spin splitting$^2$. As evidence for bright-dark excitons in bilayer WSe$_2$, we observe a decrease of the K-K intensity with decreasing temperature consistent with reduced thermalization from dark to bright excitons$^{2-4}$ (Supplementary Figure S6). We fit the measured integrated PL intensity as a function of temperature to the expression $I_{PL}(T)/I_{PL}(0) - 1 = C \exp(-E_D/k_BT)$, where $I_{PL}(T)$ is the measured intensity as a function of temperature, $I_{PL}(0)$ 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$_2$$^5$. We expect a similar value for bilayer WSe$_2$ due to the limited effect of layer-layer interactions on the band structure near the K-point of the Brillouin zone.
**Supplementary Figure S6.** Spectrally integrated PL of the A exciton emission as a function of temperature for both circular polarizations when excited with a 2.04 eV laser. The drop in emission intensity with temperature is consistent with a dark exciton ground state. The fitting is described in the text.
4. **Temperature-dependent polarization with varying thickness in WSe₂**

For a fixed temperature, if we increase the WSe₂ thickness to three or four layers, the K-Λ conduction band difference should become smaller. Similarly, the onset of an increase in DOCP should occur at a higher temperature compared to a bilayer. We confirm this trend by measuring the emission DOCP for three and four layers of WSe₂ and by comparing it as a function of temperature to that of a bilayer (Supplementary Figure S7).

![Graph showing temperature-dependent DOCP measurements for 1, 2, 3, and 4 layers of WSe₂ showing an increase in the onset temperature of DOCP with increasing layer thickness.](image)

**Supplementary Figure S7.** Temperature-dependent DOCP measurements for 1, 2, 3, and 4 layers of WSe₂ showing an increase in the onset temperature of DOCP with increasing layer thickness. The 2, 3, and 4 layer data was acquired using 2.04 eV excitation. The monolayer data was acquired using 1.796 eV excitation. The fits are made by assuming a Boltzmann distribution for the K-K’ intervalley scattering, see details in the main text.

**References**

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