Intervalley Scattering of Interlayer Excitons in a MoS$_2$/MoSe$_2$/MoS$_2$ Heterostructure in High Magnetic Field

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Abstract

Degenerate extrema in the energy dispersion of charge carriers in solids, also referred to as valleys, can be regarded as a binary quantum degree of freedom, which can po-
tentially be used to implement valleytronic concepts in van der Waals heterostructures based on transition metal dichalcogenides. Using magneto-photoluminescence spectroscopy, we achieve a deeper insight into the valley polarization and depolarization mechanisms of interlayer excitons formed across a MoS$_2$/MoSe$_2$/MoS$_2$ heterostructure. We account for the non-trivial behavior of the valley polarization as a function of the magnetic field by considering the interplay between exchange interaction and phonon mediated intervalley scattering in a system consisting of Zeeman-split energy levels. Our results represent a crucial step towards the understanding of the properties of interlayer excitons, with strong implications for the implementation of atomically thin valleytronic devices.

**Keywords**

Transition metal dichalcogenides, van der Waals heterostructures, interlayer exciton, magnetophotoluminescence, valley polarization

In close analogy with spin and its use in quantum information processing, the valley pseudospin can potentially be used to encode, store and transfer information. While valley physics has been investigated in a variety of materials, including AlAs, silicon, diamond, bismuth, and graphene, the lack of a direct band gap in these systems precludes optically addressing and reading out the valley degree of freedom. In monolayer transition metal dichalcogenides (TMDs), the valley degree of freedom corresponds to a direct band gap in the visible range at the nonequivalent but degenerate K$^+$ and K$^-$ points of the Brillouin zone. This, along with the locking of the spin and valley degrees of freedom, allows to optically initialize, manipulate and read out the valley pseudospin using circularly polarized light. The large exciton binding energy in these materials is reflected in a very large dipole moment, which induces sub-ps radiative lifetimes. This, combined with very efficient intervalley scattering mediated via electron-hole exchange interaction, strongly limits their usefulness of monolayer TMDs in practical valleytronic devices for quantum
information science.

A possibility to overcome these limitations is offered by van der Waals heterostructures, obtained by vertically stacking monolayers of different TMDs. Photoexcited charge carriers are quickly separated\textsuperscript{16} due to the type II band alignment exhibited by heterobilayers\textsuperscript{17}, forming a quasiparticle referred to as interlayer exciton. The spatial separation of the charges leads to a significant increase (up to five order of magnitudes, $\sim 100$ ns) of the recombination life time of interlayer excitons\textsuperscript{18,19}. Moreover, in analogy to intralayer excitons, valley polarization of interlayer excitons can be injected via optical means. The reduced spatial overlap of the electron-hole wavefunctions leads to a dramatically decreased electron-hole exchange interaction, which results in long-lived valley polarization (up to 40 ns)\textsuperscript{20}. These properties make interlayer excitons, formed across van der Waals heterostructures, ideally suited for valleytronic applications.

The manipulation of the valley degree of freedom via the application of magnetic field has been successfully demonstrated for intralayer excitons\textsuperscript{21–25}. This approach has recently been extended to interlayer excitons, where the observation of a giant valley Zeeman splitting and a subsequent near-unity valley polarization has been enabled by the 60° tilt angle between mechanically exfoliated MoSe\textsubscript{2}/WSe\textsubscript{2} monolayers\textsuperscript{26}. However, a fundamental understanding of the dynamics of the interlayer exciton population as well as valley depolarization mechanism is still lacking.

Here, we achieve a deeper insight into the properties of interlayer excitons by performing detailed magneto-photoluminescence (magnetoPL) spectroscopy of a heterostructure formed by MoS\textsubscript{2} and MoSe\textsubscript{2} monolayers\textsuperscript{19,27}. The materials which compose our heterostructures are lattice mismatched. This leads to the formation of a moiré pattern\textsuperscript{28,29}, which has been shown to influence the electronic and valley properties of interlayer excitons\textsuperscript{30–32}. We lift the valley degeneracy by applying magnetic fields up to 28 T in the Faraday configuration. We observe a population imbalance in the Zeeman split valleys, which allows us to precisely control the valley polarization from 0 to almost 100% by applying the magnetic field. For
the first time, we describe the magnetic field dependence of the valley polarization of a van
der Waals heterostructure by a model, which accounts for the observed intervalley relaxation
via an interplay between exchange and phonon driven intervalley scattering in Zeeman split
levels.

The zero field PL and reflectivity contrast spectra of our structure are presented in the
Supporting Information. The PL spectrum consists of sharp peaks attributed to the recombina-
tion of free and charged intralayer excitons in MoS$_2$ and MoSe$_2$,\textsuperscript{27} and a low energy peak
at $\sim 1.38$ eV, which results from the radiative recombination of the interlayer exciton.\textsuperscript{19} The
red shifted interlayer exciton in our heterostructure as compared to a mechanically exfoliated
MoS$_2$/MoSe$_2$ bilayer deposited on SiO$_2$\textsuperscript{33} could be partially attributed to the larger dielectric
screening induced by sapphire. This is consistent with the trend observed in TMD monolayers
when additional dielectric screening was purposefully introduced.\textsuperscript{34} The magnetoPL is
excited with circularly or linearly polarized light, and is detected using a circular polarization
basis. A representative set of magnetoPL spectra of the interlayer exciton is presented
in Fig. 1(b). The PL peak exhibits a significant Zeeman splitting and a considerable valley
polarization, which increases with increasing magnetic field and saturates for $B > 20$ T. The
slightly lower scaling factor for $B = 24$ T results from a small deviation from the saturated
valley polarization reached at high fields, due to experimental uncertainties (see, e.g., the
valley polarization in Fig. 2 and the valley polarization extracted from the data of Fig. 1(b)
shown in Fig. S4(c), Supporting Information). To analyze quantitatively our data, we fit a
single Gaussian function to the PL spectra of the interlayer exciton and extract the emission
energies, which are plotted in Fig. 1(c) as a function of the magnetic field. The Zeeman shift
of the $\sigma^+$ polarization is larger than that of the $\sigma^-$ polarization. This is a consequence of
the diamagnetic effect – quadratic in magnetic field – which blue shifts the exciton energy.\textsuperscript{35}
The observation of the diamagnetic shift reflects the relatively large electron hole separation
and will be subject of a separate study. The energy difference between the two polarizations
is shown in Fig. 1(d), where a very large valley Zeeman splitting of $\sim 25$ meV at the highest
magnetic field is observed. In analogy with the standard analysis for intralayer excitons, we define $\Delta E = E_{\sigma^+} - E_{\sigma^-} = g_{\text{eff}} \mu_B B$, where $g_{\text{eff}}$ denotes the effective interlayer exciton $g$-factor, $\mu_B \sim 58 \, \text{meV/T}$ the Bohr magneton, and $B$ the magnetic field. The fitting of the data of Fig. 1(d) gives $g_{\text{eff}} = -13.1 \pm 0.5$. We estimated $g_{\text{eff}}$ also with the center of mass method\textsuperscript{22} (see Supporting Information for a more detailed discussion of the fitting procedures and for the corresponding plots), which yielded $g_{\text{eff}} = -13.4 \pm 0.5$, identical within experimental error to the value determined by fitting. This very large $g_{\text{eff}}$ has been interpreted as stemming from a non-vanishing valley orbital contribution to the overall magnetic moments of the bands for heterostructures with a $60^\circ$ stacking angle.\textsuperscript{26} This configuration makes transitions between bands with different valley indexes optically bright, as shown in Fig. 1(a) and discussed more in detail in the Supporting Information. In our heterostructure, the moiré pattern yields locally an AB configuration of the registry of the central MoSe\textsubscript{2} layer with one of the two MoS\textsubscript{2} layers, effectively similar to a lattice matched heterobilayer with $60^\circ$ stacking angle. These spots are expected to be optically bright,\textsuperscript{31,32} and to exhibit a large Zeeman splitting, consistent with the data summarized in Fig. 1. The smaller $g_{\text{eff}}$ observed here, compared with that of a MoSe\textsubscript{2}/WSe\textsubscript{2} heterostructure, is consistent with the smaller difference of the effective mass of the constituents of our sample.\textsuperscript{36,37}

As seen in Fig. 1(b), applying a magnetic field results in a sizable difference of the PL intensities of the interlayer exciton recorded in $\sigma^+$ and $\sigma^-$ polarizations. For a quantitative analysis, we define the degree of circular polarization as $P_c = (I^+ - I^-)/(I^+ + I^-)$, where $I^\pm$ denote the PL intensities in $\sigma^\pm$ polarizations, respectively. In Fig. 2, we plot the magnetic field dependence of $P_c$, for excitation in resonance with the A-exciton of the MoSe\textsubscript{2} monolayer for (a) linear, (b) $\sigma^-$, and (c) $\sigma^+$ excitation polarization. In the case of intralayer excitons, for an excitation with circularly polarized light, at $B = 0$ T we expect $P_c \neq 0$, which results from the optical orientation of the valley pseudospin.\textsuperscript{9,38,39} This effect has been also observed in heterobilayers\textsuperscript{20} and in our trilayer sample.\textsuperscript{19} In Fig. 2(b,c), the observed optically oriented polarization at $B = 0$ T is very small, but it is recovered by applying a
small field and already at 1 T $P_c \approx \pm 0.3$ for $\sigma^\pm$ excitation polarizations, respectively. The observed polarization is opposite to the polarization of the excitation beam, in agreement with our recent report.\textsuperscript{19} This counterpolarized emission might be due to the effects of the moiré pattern, which only locally preserves the threefold symmetry of the original crystals.\textsuperscript{31,32} A local AB stacking (corresponding to a 60° stacking angle and consistent with the observations of Fig. 1) represents a local potential minimum for the interlayer exciton, and it is characterized by a large oscillator strength of the interlayer exciton transition. It also couples to circularly polarized light of opposite helicity with respect to that of the excitation laser.\textsuperscript{31,32} A possible explanation of the opposite polarization is that the optical excitation creates intralayer excitons in the monolayers. The charge carriers are rapidly separated,\textsuperscript{16} forming interlayer excitons across the heterostructure, which relax to minima of the potential induced by the moiré pattern. These locations correspond to optically bright spots and
couple primarily to light of opposite polarization.\textsuperscript{31,32}

As the field is further increased, $P_c$ increases and at $B > 20\,\text{T}$ reaches $P_c \approx 1$ regardless of excitation polarization. Nonzero $P_c$ originates from an occupation difference between the interlayer exciton states in different valleys. In the following, we label these states as pseudospin up $|\uparrow\rangle$ and down $|\downarrow\rangle$, neglecting for the sake of simplicity the complicated spin/valley structure of the recombining interlayer exciton states depicted in Fig. 1(a). As the field is increased, the population imbalance increases due to the preferential occupation of the lower lying Zeeman state (the $|\uparrow\rangle$ state). If thermal equilibrium is established between the interlayer exciton system and the lattice, $P_c$ is determined solely by the effective $g$-factor of the interlayer exciton and by the lattice temperature. The dashed line in Fig. 2(a) shows the magnetic field dependence of this polarization, given by $P^{\text{eq}}_c = \tanh(\Delta E/(2k_B T))$, where $\Delta E$ is the Zeeman splitting between $|\downarrow\rangle$ and $|\uparrow\rangle$ states and $T = 4.5\,\text{K}$ is the bath temperature. The discrepancy between the experimental results shown in Fig. 2(a) and $P^{\text{eq}}_c$ visible at $B \lesssim 15\,\text{T}$ suggests that either the equilibrium is not established or the interlayer exciton system is characterized by a spin temperature significantly larger than 4.5 K. Even though the interlayer exciton energy (and/or its $g$-factor) suffers from inhomogeneous broadening, we find its impact negligible on the expected equilibrium $P_c$.

![Figure 2](image)

**Figure 2:** Magnetic field dependence of $P_c$ for (a) linearly polarized, (b) $\sigma^-$ and (c) $\sigma^+$ polarized excitation. The dashed gray line shows the expected evolution of the circular polarization for an exciton population fully thermalized with the lattice. The measured circular polarization (symbols) is fitted with results of a three level rate equations model (lines).
In order to determine the underlying relaxation processes responsible for the observed field dependence of $P_c$, we employ a four-level rate equation model depicted schematically in Fig. 3 (see Supporting Information for further details). The solution of this model provides the field dependence of the interlayer exciton populations $n_\uparrow$ and $n_\downarrow$ of the Zeeman split $|\uparrow\rangle$ and $|\downarrow\rangle$ states. Assuming that $P_c = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, we find:

$$P_c = P_0 \frac{\gamma}{\gamma + \gamma_d + \gamma_u} + \frac{\gamma_d - \gamma_u}{\gamma + \gamma_d + \gamma_u},$$

(1)

where $\gamma_{u,d}$ are intervalley scattering rates (see Fig. 3) and $\gamma$ denotes the recombination rate. The first term describes the optically created polarization, in which $P_0$ is the polarization transferred from the circularly polarized excitation. The second term describes the tendency of the system to reach thermal equilibrium. The intervalley scattering rates can be written as:

$$\gamma_{u,d} = \frac{1}{\tau_{v0}} \frac{\Gamma^2}{\Gamma^2 + \Delta E^2} + \frac{\alpha \Delta E^3}{\exp\left(\frac{\pm\Delta E}{k_B T}\right) - 1},$$

(2)

where the first term describes the effect of the electron-hole exchange interaction, which acts as an effective in-plane magnetic field on the valley pseudospin with a zero-field intervalley relaxation time $\tau_{v0}$. The precession of the valley pseudospin around this effective field, together with the reorientation of this field due to momentum scattering, induces the intervalley scattering. However, this is a zero-energy process and thus it is only efficient when the two valley states $|\uparrow\rangle$ and $|\downarrow\rangle$ are close in energy. Therefore this resonant process is controlled by the width parameter $\Gamma$. As the Zeeman splitting $\Delta E$ is increased, the exchange-driven relaxation slows down and becomes negligible when the field-induced splitting $\Delta E$ becomes much larger than $\Gamma$. The second term in Eq. (2) describes the one-phonon spin-lattice relaxation process, which requires an emission or an absorption of a phonon, if the scattering occurs to the lower ($\gamma_d$) or higher ($\gamma_u$) valley, respectively. Consequently, the scattering rates are proportional to the phonon Bose occupation factors $n_k + 1$ or $n_k$, respectively. In Eq. (2), $\alpha$ is a measure of the exciton-phonon coupling strength, independent
of $\Delta E$.

Figure 3: Schematic of the rate equations model for the case of $\sigma^+$ excitation. Dashed and solid horizontal lines denote the relevant exciton states at $B = 0$ T and at $B > 0$ T, respectively. A laser beam creates excitons in K$^+$ valley of one of the constituent monolayers. The type-II band alignment in the heterostructure leads to an ultrafast charge separation and creation of an interlayer exciton. This process is denoted by dashed arrows. The recombination of the interlayer exciton, denoted by thick, straight arrows, occurs with a rate $\gamma$ and competes with intervalley scattering, denoted by curved thin arrows, occurring with rates $\gamma_u$ and $\gamma_d$ for the scattering upward and downward in energy, respectively.

We evaluate experimentally the recombination rate $\gamma$ by measuring the time-resolved PL of the interlayer exciton. The temporal decays of the PL signal are shown in Fig. 4(a). The PL decays are fitted well with a biexponential function. The short decay time obtained from the fitting, $\tau_{\text{short}}$, presented in Fig. 4(b), is about 16 ns, and insensitive to the magnetic field. The fitted long decay time, $\tau_{\text{long}}$, as shown in Fig. 4(b), decreases from about 700 ns to 350 ns over the investigated field range. In agreement with previous reports, both decay times are 3–5 orders of magnitude longer than the decay of excitonic PL from a monolayer, a consequence of the spatial separation of the electron and the hole. The shortening of $\tau_{\text{long}}$ with increasing magnetic field can be attributed to the magnetic field induced shrinking of the exciton orbital wave function. Due to a small time window of 350 ns available to detect the PL in these experiments, the evaluation of the long decay time is subject to significant errors.

For the purpose of fitting the field dependence of $P_c$ with our model calculations, we define an average decay time as $\tau_{\text{avg}} = (A_{\text{long}}\tau_{\text{long}} + A_{\text{short}}\tau_{\text{short}})/(A_{\text{long}} + A_{\text{short}})$, where $A_{\text{long}}$ and $A_{\text{short}}$ are the amplitudes of the long and short decays, respectively, and assume that
\( \gamma = 1/\tau_{\text{avg}} \). To obtain \( \gamma \) for all the fields at which \( P_c \) was recorded, we interpolate the field dependence of \( \tau_{\text{avg}} \) with an exponential function (see Supporting Information).

The fitting of the model is performed globally to the three sets of data presented in Fig. 2(a-c). The fitting parameters are \( \tau_{\nu 0} \), \( \Gamma \), \( \alpha \), and the transferred polarization \( P_0 = 0 \) for linear excitation and \( \mp P_0 \) for \( \sigma^+ \) and \( \sigma^- \) excitations, respectively. The agreement between the fitted curves (solid lines in Fig. 2(a-c)) and the experimental data is very good, which allows us to reconstruct the field-induced changes of the intervalley scattering rates. At fields \( \ll 1 \text{T} \), the optically created valley polarization is quenched by the exchange-driven process.\(^{44}\) In TMD monolayers, this process leads to intervalley scattering times of the order of a few ps.\(^{14}\) In heterostructures, due to the spatial separation of the electron and the hole, the efficiency of this process is dramatically reduced. The zero-field intervalley relaxation time obtained from our fitting is \( \tau_{\nu 0} = 40 \text{ns} \), four orders of magnitude larger than that of excitons in a WSe\(_2\) monolayer\(^{14}\) and similar to the values reported for a WSe\(_2\)/MoSe\(_2\) heterostructure.\(^{29}\) As the field is increased up to \( \sim 5 \text{T} \), the exchange-driven mechanism is suppressed and the optically created polarization is recovered. Thus, for \( \sigma^\pm \) excitations, \( P_c \) becomes negative or positive, respectively, and our fitting yields \( P_0 = \mp 0.29 \). The value of \( \Gamma \) obtained from the fitting is 40\( \mu\text{eV} \). This value is much smaller than the line width of the interlayer transition, which suffers from a strong inhomogeneous broadening caused most probably by the laterally varying distance between the monolayers constituting the heterostructure and resulting from residual adsorbates between them. Also, the obtained \( \Gamma \) is smaller than the exciton homogeneous linewidth measured for monolayer WSe\(_2\).\(^{13}\) We remark that a similar recovery of the optically created valley polarization was observed for long-lived localized excitons in monolayer tungsten dichalcogenides.\(^{47}\) The recovery was attributed to a suppressed intervalley scattering of dark excitons. This mechanism might contribute to the recovery of the polarization in our heterostructure, given that the optically active AB stacking mimics the band structure of W-based TMDs, with dark exciton states lying energetically below the bright ones.\(^{48}\) The recovery of \( P_c \) at small fields suggests that
the spin-lattice relaxation is slower than the recombination in that magnetic field range, which leads to a non-equilibrium occupations of the interlayer exciton states. As the field is increased above $\sim 5 \text{T}$, the rate of spin-lattice relaxation increases and drives the system towards equilibrium. Our model assumes that for $\Delta E \gg k_B T$, the intervalley scattering rate increases as $\Delta E^3$. When this rate becomes larger than $\gamma$, the $P_c$ becomes positive and no longer determined by the excitation polarization. Our fitting yields $\alpha = 5 \text{ns}^{-1} \text{eV}^{-3}$. A very similar value was obtained for excitons in GaAs quantum wells, which is a surprising coincidence since we would expect a stronger exciton-phonon coupling in TMDs.

Using Eq. 2 and our fitted parameters, we calculate the field dependence of the inter-valley scattering time as $\tau_v = 1/(\gamma_d + \gamma_u)$ and compare it to the interpolated average recombination time $\tau_{\text{avg}}$ in Fig. 4(c). As inferred from the analysis of the evolution of $P_c$ with magnetic field, $\tau_v < \tau_{\text{avg}}$ at $B < 1 \text{T}$, where the exchange-driven process dominates. Then, in the intermediate field range $1 \text{T} \leq B \lesssim 7 \text{T}$, $\tau_v$ becomes larger that $\tau_{\text{avg}}$. Above $\sim 7 \text{T}$, the intervalley scattering time decreases below the recombination time due to the increased Zeeman splitting $\Delta E$, and the interlayer exciton system is driven toward thermal equilibrium, as evidenced by the experimental data which approach the dashed curve in Fig. 4.

Figure 4: (a) Temporal decays of the interlayer exciton PL for various magnetic fields plotted together with fitted biexponential decay functions. (b) Magnetic field dependence of the short and long decay times. (c) Comparison between the intervalley scattering time $\tau_v$ and the recombination time $\tau_{\text{avg}}$. The contributions to the intervalley scattering from the exchange-driven process and the spin-lattice relaxation process are also shown. $\tau_{\text{avg}}$ is interpolated from the measured PL decay times.
In conclusion, we have performed detailed magnetoPL spectroscopy of interlayer excitons formed in a MoS\textsubscript{2}/MoSe\textsubscript{2}/MoS\textsubscript{2} heterostructure. The effective $g$-factor of the interlayer exciton is significantly larger as compared to that of intralayer excitonic transitions, due to a non-vanishing contribution of the valley orbital moments. The large electron-hole separation in the interlayer exciton results in the suppression of intervalley scattering, which is directly reflected in our polarization resolved measurements. At zero magnetic field, the polarization degree is mainly determined by the intervalley scattering driven by the electron-hole exchange interaction. A small magnetic field can efficiently suppress this mechanism, which results in a recovery of the optically induced polarization. In the high field limit, the PL polarization is dominated by the thermal occupation of Zeeman split states and does not depend on the injected polarization. The interplay between exchange interaction, phonon driven scattering and magnetic field can result in non-monotonic behavior of the valley polarization. Our results represent a crucial step for the implementation of valleytronic concepts based on interlayer excitons by providing a thorough insight into the valley polarization generated via an applied magnetic field and the competing depolarization mechanisms.

**Methods**

*Sample preparation.* The large area MoS\textsubscript{2} and MoSe\textsubscript{2} monolayer films, which form the investigated heterostructure, were grown separately by chemical vapor deposition (CVD) on sapphire substrates.\textsuperscript{49,50} The heterostructure was fabricated by two sequential KOH-based transfer steps.\textsuperscript{51} The first transfer allowed to form a MoS\textsubscript{2}/MoSe\textsubscript{2} heterobilayer, which was subsequently transferred onto a MoS\textsubscript{2} film to form the trilayer stack.\textsuperscript{27} This approach allowed us to obtain multiple van der Waals heterostructures with varying stacking angles over very large areas.\textsuperscript{19,27}

*Magneto-optical spectroscopy.* The sapphire substrate with large area heterostructures was mounted on a $x - y - z$ translation stage driven by piezoelectric actuators and cooled...
down at 4.5 K in a liquid helium cryostat. Static magnetic fields up to 28 T were applied making use of a water cooled resistive magnet. The PL was excited by a diode laser emitting at 640 nm (excitation in resonance with the MoS$_2$ A-exciton) or a Ti:sapphire laser tuned at 740 nm (excitation in resonance with the MoSe$_2$ A-exciton). The typical excitation power was kept as low as possible and in any case lower than 30 µW. The excitation laser was circularly or linearly polarized with a linear polarizer and a Babinet-Soleil compensator. The beam was focused on the sample by a long working distance microscope objective, which was also used to collect the PL. This signal was analyzed in a circular polarization basis with a zero-order quarter-waveplate and a linear polarizer and dispersed by a 0.3 m long monochromator coupled to a liquid nitrogen cooled CCD detector. Time resolved magnetoPL was measured by operating the diode laser in pulsed mode with a repetition frequency of 2.5 MHz, synchronized with a Si avalanche photodiode. The PL was spectrally selected by making use of a longpass filter.

**Supporting Information Available**

The following files are available free of charge. Low temperature µPL spectra of a Mo$_2$/MoSe$_2$/MoS$_2$ heterostructure at zero magnetic field, estimation of valley Zeeman splitting for intralayer and interlayer excitons, additional details concerning the fitting procedures used for the determination of the PL energy, four level rate equation model and magnetic field dependence of the valley polarization for an excitation in resonance with the A exciton of MoS$_2$.

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Conflict of interest disclosure

The authors declare no competing financial interest.

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