Long-lived spin polarization in n-doped MoSe$_2$ monolayers

M. Schwemmer, P. Nagler, A. Hanninger, C. Schüller, and T. Korn

Institut für Experimentelle und Angewandte Physik, Universität Regensburg, D-93040 Regensburg, Germany

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Transition metal dichalcogenide monolayers are highly interesting for potential valleytronic applications due to the coupling of spin and valley degrees of freedom and valley-selective excitonic transitions. However, ultrafast recombination of excitons in these materials poses a natural limit for applications, so that a transfer of polarization to resident carriers is highly advantageous. Here, we study the low-temperature spin-valley dynamics in nominally undoped and n-doped MoSe$_2$ monolayers using time-resolved Kerr rotation. In the n-doped MoSe$_2$, we find a long-lived component of the Kerr signal which we attribute to the spin polarization of resident carriers. This component is absent in the nominally undoped MoSe$_2$. The long-lived spin polarization is stable under applied in-plane magnetic fields. Spatially resolved measurements allow us to determine an upper bound for the electron spin diffusion constant in MoSe$_2$.

Transition metal dichalcogenide (TMDC) monolayers have a peculiar band structure [1], in which spin and valley degrees of freedom are coupled, and the optical selection rules allow for valley-selective generation of excitons [2]. An excitonic valley polarization can be read out optically via the circular polarization degree of the emitted photoluminescence (PL), and initial studies using continuous-wave excitation revealed a large steady-state polarization [3]. While many early studies of valley physics focused on the naturally abundant MoS$_2$, synthetic TMDC crystals quickly garnered scientific attention due to their spectrally narrow PL emission [4] and the large tuning range of conduction- and valence-band spin splitting [5], which was shown to be stable against depolarization in large in-plane magnetic fields [6].

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Among the TMDC family, MoSe$_2$ is characterized by a comparatively low optically induced valley polarization degree, which is only observable at all under near-resonant excitation conditions [7], and can be increased by modifying the recombination dynamics using coupling to photonic cavities [8]. To investigate the anomalously low valley polarization in MoSe$_2$, time-resolved studies of valley dynamics are needed.

Here, we directly compare the low-temperature spin-valley dynamics in nominally undoped and n-doped MoSe$_2$ monolayers using time-resolved Kerr rotation (TRKR). We find a long-lived component of the Kerr signal in the n-doped MoSe$_2$ which is absent in the nominally undoped sample. We attribute this to an optically induced spin polarization of resident carriers. TRKR measurements in an applied in-plane magnetic field show no influence of the field on this spin polarization, indicating that it is stabilized by the large, valley-contrasting conduction-band spin splitting of MoSe$_2$.

The investigated samples are prepared from bulk crystals (deliberately n-doped MoSe$_2$ supplied by 2D semiconductors and MoSe$_2$ without intentional doping and unspecified majority carrier type supplied by HQ graphene) by mechanical exfoliation. For this, we use Gel-Film™ pieces (Gelpak) as an intermediate substrate, and suitable monolayer flakes are then stamped onto the final substrate (silicon covered with a 285 nm SiO$_2$ layer and pre-defined metal markers) using an all-dry transfer technique [9]. The investigated samples are identified as HQ (monolayer flake prepared from HQ graphene MoSe$_2$ bulk crystal) and n-2D (monolayer flake prepared from n-doped 2D semiconductors MoSe$_2$ bulk crystal) throughout the manuscript. PL and time-resolved PL (TRPL) measurements are performed in a self-built microscope setup, details are described elsewhere [10]. The time resolution of the streak camera used for the TRPL measurements is below 10 ps. Details of the setup for the TRKR measurements are described in Ref. 20. Briefly, a mode-locked Ti:Sapphire laser emitting 100 fs pulses is used as the source for pump and probe beams. Band pass filters cut non-overlapping high-energy (pump) and low-energy (probe) regions out of the broad laser spectrum. A mechanical delay stage is used to define the time delay $\Delta t$ between pump and probe pulses. Pump and probe beams are collinearly focused via a 100x microscope objective onto the sample, yielding spot diameters of about 1.5 $\mu$m and excitation densities of about 9 kWcm$^{-2}$ (pump) and 27 kWcm$^{-2}$ (probe), respectively. The pump pulses are circularly polarized to generate a spin-valley polarization, while the probe pulses are linearly polarized to probe this polarization via the magneto-optical Kerr effect. The pump beam is filtered out from the back-reflected light by a long-pass

[1] Electronic mail: tobias.korn@physik.uni-regensburg.de
FIG. 1. (a) Time-integrated PL spectra measured on n-2D (red lines) and HQ (black lines) samples at 4.5 K. The shaded areas indicate the energetic positions and linewidth of the pump (orange) and probe (blue) pulses used in the TRKR measurements. The inset shows a small region of the same spectra around the exciton (X) and trion (X\(^{-}\)) peaks, with the energy differences between the X and (X\(^{-}\)) peaks indicated by the black scale bars. (b) Time-resolved PL traces measured on n-2D (red) and HQ (black) samples at 4.5 K. Solid (dashed) lines indicate traces centered around trion (exciton) PL peaks. The inset shows a false-color plot of the time- and spectrally resolved PL of the HQ sample measured at 4.5 K.
The exciton and trion states, the valley dephasing mechanism based on long-range exchange interaction is highly efficient and compatible with the few-picosecond decay times we observe. Remarkably, the TRKR traces measured on the n-2D sample show a very different behavior: as seen in Fig. 2(c), the traces are very stable as a function of lab time, with the initial trace closely matching subsequent traces. All measurements show a substantial long-lived component, which significantly exceeds the measurement window of about 1 ns limited by the mechanical delay stage of our experiment, as shown in Fig. 2(d). On the few-picosecond timescale, the decay of the signal is well-described by a biexponential decay function with a constant offset corresponding to the long-lived component. The fast and slow components of this fit yield values of $t_1=1.3$ ps and $t_2=6$ ps, respectively, demonstrating faster dephasing than in the HQ sample, which might stem from increased scattering of excitons and trions with the large resident carrier density in this sample. On the long timescale shown in Fig. 2(d), we also utilize a biexponential decay function with a constant offset to account for the very long-lived component that exceeds our measurement window. While the fast $t_1$ dynamics observed on the few-ps timescale are not visible in this dataset, which was recorded with a 3 ps step size, we find a similar decay constant $t_2=6$ ps, and an additional, slower component of $t_3=395$ ps. The constant offset amounts to about 25 percent of the initial TRKR amplitude. Using the noise level of the TRKR signal before arrival of a pump pulse as a lower boundary for the TRKR signal remaining after 12 ns (corresponding to the repetition rate of the laser), we can determine an upper limit for the lifetime of the Kerr signal exceeding the time window available in our experiment, and we find a value of $t_F=3.6$ ns. Since the lowest-energy excitonic state in MoSe$_2$ is bright, in contrast to the tungsten-based materials, where dark excitons and trions can contribute to a long-lived valley polarization, we associate the long-lived component with a spin polarization of the resident carriers in the deliberately n-doped n-2D sample. This assertion is supported by the absence of such a long-lived component in the HQ sample with its lower carrier density. For these resident carriers, the long-range exchange mechanism responsible for exciton valley dephasing is absent, and naturally, the PL lifetime does not pose an upper limit for the spin polarization of resident carriers, as the direct comparison of PL dynamics and Kerr rotation trace in Fig. 2(d) confirms. The lifetime we observe is in agreement with calculations for the electron spin lifetime in MoSe$_2$ at low temperatures. In order to initialize a resident spin polarization using optical excitation, a transfer of polarization from excitons to resident carriers has to occur, in which a subset of the optically generated holes dephases during exciton formation, so that unpolarized excitons are formed using the resident carrier reservoir, while a larger subset of the optically oriented electrons retains its polarization. Such an asymmetric dephasing may be driven by different electron and hole spin-flip scattering rates with the resident carriers, or by

![FIG. 2. (a) TRKR traces measured HQ sample at 4.5 K as a function of lab time. The traces are shifted vertically with respect to each other. (b) Additional TRKR traces measured on same position of HQ sample as in (a), about 20 minutes after initial illumination of this sample position. (c) TRKR traces measured on n-2D sample at 4.5 K as a function of lab time. (d) Normalized TRKR (red) and trion TRPL (blue) traces measured on n-2D sample at 4.5 K. The solid black line indicates a biexponential fit to the TRKR data. The dark green dotted line indicates the offset level of the biexponential fit.](image-url)
different spin dephasing rates during energy relaxation in the conduction and valence bands, which are common, e.g., in GaAs-based heterostructures.

To explore the stability of this resident spin polarization, we perform measurements in an applied in-plane magnetic field of 250 mT (the maximum field available in our electromagnet). As Fig. 3(a) shows, there is neither any discernible spin precession observable, nor is there a significant change of the decay of the Kerr signal as compared to the zero-field measurement under similar experimental conditions. This result is in contrast to the resident carrier spin dynamics in the related material MoS$_2$, where a significant increase of the decay rate with magnetic field, combined with an oscillatory behavior, was observed. This qualitative difference stems from the larger conduction-band spin splitting of MoSe$_2$ (20 meV compared to 3 meV in MoS$_2$), which effectively acts as a large, valley-dependent out-of-plane magnetic field, suppressing spin precession about the applied in-plane magnetic field and stabilizing the spin polarization. A qualitatively similar behavior was also reported for resident spin polarization in WS$_2$.

Finally, we perform spatially resolved experiments, where the pump beam is scanned across the sample surface along a line, while the position of the probe beam is kept fixed. Figure 3(b) shows the Kerr signal as a function of pump-probe beam distance for 3 different time delays between pump and probe. Naturally, the signal is maximum for overlapping pump and probe beams and decays with increasing distance, following a convolution of pump and probe beam spatial profiles. We find that the absolute signal amplitude decreases with increasing time delay, indicating the decay of the spin polarization. However, the width of the curve (extracted via fitting a Gaussian to the data) does not increase significantly as a function of time delay, indicating that spin diffusion of resident carriers is below our detection limit. Using the spatial resolution of our setup and the available time window, we can estimate an upper boundary for the spin diffusion constant of $15 \text{ cm}^2/\text{s}$.

In conclusion, we have investigated the spin-valley dynamics in different MoSe$_2$ monolayer samples using time-resolved Kerr rotation. In an intentionally n-doped sample, we observe a long-lived component of the Kerr signal which is absent in a nominally undoped MoSe$_2$ sample. We attribute this signal to a spin polarization of the resident electrons, which is established via optical excitation and subsequent transfer of polarization to resident carriers. Spatially resolved measurements allow us to determine an upper boundary for the electron spin diffusion constant. The long-lived electron spin polarization is stable against in-plane magnetic fields due to the large conduction-band spin splitting of MoSe$_2$, making n-doped MoSe$_2$ potentially interesting for valleytronic devices.

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17. T. Godde, D. Schmidt, J. Schmutzler, M. Aßmann, J. Debus, F. Withers, E. M. Alexeev, O. Del Pozo-Zamudio, O. V. Skrypka, K. S. Novoselov, M. Bayer, and A. I. Tartakovskii, Physical Review B 94, 165301 (2016).
18. L. Yang, N. A. Sinitsyn, W. Chen, J. Yuan, J. Zhang, J. Lou, and S. A. Crooker, Nature Physics 11, 830 (2015).
19. E. J. Bushong, Y. Luo, K. M. McCreary, M. J. Newburger, S. Singh, B. T. Jonker, and R. K. Kawakami, arXiv:1602.03568 (2016).
20. G. Wang, E. Palleau, T. Amand, S. Tongay, X. Marie, and B. Urbaszek, Applied Physics Letters 106, 112101 (2015).
21. G. Kioseoglou, A. T. Hanbicki, M. Currie, A. L. Friedman, and B. T. Jonker, Scientific Reports 6, 25041 (2017).
22. M. Baranowski, A. Surrente, D. K. Maude, M. Ballottin, A. A. Mitioglu, P. C. M. Christianen, Y. C. Kung, D. Dumcenco, A. Kis, and P. Plochocka, 2D Materials 4, 025016 (2017).
23. N. Lundt, P. Nagler, A. Naditov, S. Klembt, M. Wurdack, S. Stoll, T. H. Harder, S. Betzold, V. Baumann, A. V. Kavokin, C. Schüller, T. Korn, S. Höfling, and C. Schneider, 2D Materials 4, 025096 (2017).
24. A. Castellanos-Gomez, M. Buscema, R. Molenaar, V. Singh, L. Janssen, H. S. J. van der Zant, and G. A. Steele, 2D Materials 1, 011002 (2014).
25. P. Nagler, G. Plechinger, M. V. Ballottin, A. Mitioglu, S. Meier, N. Paradiso, C. Strunk, A. Chernikov, P. C. M. Christianen, C. Schüller, and T. Korn, 2D Materials (2017).
26. M. Schwemmer, A. Hanninger, M. Weingartner, M. Oltscher, M. Ciorga, D. Weiss, D. Schuh, D. Bougeard, T. Korn, and C. Schüller, Applied Physics Letters 109, 172106 (2016).
27. M. M. Glazov, Physics of the Solid State 54, 1 (2012).
28. K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, and J. Shan, Nature Materials 12, 207 (2013).
29. A. Chernikov, A. M. van der Zande, H. M. Hill, A. F. Rigosi, A. Velauthapillai, J. Hone, and T. F. Heinz, Physical Review Letters 115, 126802 (2015).
30. G. Plechinger, P. Nagler, J. Kraus, N. Paradiso, C. Strunk, C. Schüller, and T. Korn, physica status solidi (RRL) - Rapid Research Letters 9, 457 (2015).
31. M. Currie, A. T. Hanbicki, G. Kioseoglou, and B. T. Jonker, Applied Physics Letters 106, 201907 (2015).
32. B. Miller, E. Parzinger, A. Vernickel, A. W. Holleitner, and U. Wurstbauer, Applied Physics Letters 106, 122103 (2015).
33. M. M. Glazov, T. Amand, X. Marie, D. Lagarde, L. Bouet, and B. Urbaszek, Physical Review B 89, 201302 (2014).
34. T. Yu and M. W. Wu, Physical Review B 89, 205303 (2014).
35. G. Plechinger, P. Nagler, A. Arora, R. Schmidt, A. Chernikov, A. G. del Aguila, P. C. Christianen, R. Bratschitsch, C. Schüller, and T. Korn, Nature Communications 7, 12715 (2016).
36. G. Plechinger, T. Korn, and J. M. Lupton, The Journal of Physical Chemistry C 121, 6409 (2017).
37. F. Volmer, S. Pissinger, M. Ersfeld, S. Kuhlen, C. Stampfer, and B. Beschoten, arXiv:1702.03712 (2017).
38. M. Kugler, K. Korzekwa, P. Machnikowski, C. Gradl, S. Furthmeier, M. Griesbeck, M. Hirmer, D. Schuh, W. Wegscheider, T. Kuhn, C. Schüller, and T. Korn, Phys. Rev. B 84, 085327 (2011).