Anomalous rotation of the linearly polarized emission of bright excitons in strained WSe₂ monolayers under high magnetic fields

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Linearly polarized microphotoluminescence (µ-PL) measurements of strained WSe₂ monolayers in out-of-plane high magnetic fields are presented. At low temperature, a splitting of the bright exciton emission into two exciton components is observed, which is attributed to an in-plane uniaxial strain based on the full polarization dependence of the photoluminescence spectrum. High magnetic field measurements directly reveal a distinct evolution of the linear polarization and allows us to extract the valley coherence time constants (t²) for both exciton components. For the high-energy transition of the exciton, the valley coherence time t² is four times larger, ≃1.97 ps. This valley coherence time observed here may be explored for future valleytronic applications.

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I. INTRODUCTION

Two-dimensional transition-metal dichalcogenides (TMDCs), such as MoS₂, MoSe₂, WS₂, and WSe₂, have recently emerged as a promising class of semiconducting materials to investigate new physical effects related to strong Coulomb mediated electron-hole (e-h) interactions [1–3]. Due to a direct band gap located at two degenerate valleys at the corners of the hexagonal Brillouin zone (K and K′) or the energy separation between the indirect and direct gaps increases due to suppression of the phonon-induced intervalley (K-Q) scattering [20]. At cryogenic temperatures, when the exciton linewidth is smaller due to a reduced phonon-assisted broadening, a splitting of the bright exciton emission into two exciton components, each with peculiar polarization of neutral exciton emission in strained monolayer WSe₂ monolayers. Moreover, the energy separation between the indirect and direct gaps increases due to suppression of the phonon-induced intervalley (K-Q) scattering [20]. At cryogenic temperatures, when the exciton linewidth is smaller due to a reduced phonon-assisted broadening, a splitting of the bright exciton emission into two exciton components, each with peculiar polarization properties, is observed [21]. In this respect, probing linear polarization of neutral exciton emission in strained monolayer TMDCs under high magnetic fields can provide important information regarding the mechanism of valley decoherence.

We present polarized microphotoluminescence measurements on strained WSe₂ monolayers at 4.2 K in a linearly polarized basis (both in excitation and detection) in perpendicular magnetic fields up to 25 T. Control measurements are performed on unstrained monolayers. We investigate the

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degree of linear polarization of the neutral exciton emission and its field-induced rotation angle, since these are the key parameters towards the understanding of valley decoherence. At zero magnetic field, we show that the two exciton components, separated by a few meV, have optical properties that depend strongly on linear excitation polarization. Interestingly, measurements in high magnetic fields show that the two exciton components exhibit a different rotation angle and a distinct decrease of linear polarization with field. We analyze our data using a simple four-level model system and extract a valley coherence time constant of $T_{s}^{2} \simeq 0.45$ ps for the high-energy exciton, which is of the same order of magnitude as the value for an unstrained WSe$_2$ monolayer sample ($\simeq 0.34$ ps). Surprisingly, the valley coherence time constant for the low-energy exciton state is four times larger ($\simeq 1.97$ ps). Our results demonstrate that strain can be used to alter and optimize the optical properties in monolayer TMDCs, including complex effects such as valley coherence.

II. EXPERIMENT

WSe$_2$ monolayer flakes were prepared by mechanical exfoliation from bulk crystals and transferred onto 285-nm SiO$_2$/Si substrates. The monolayer region was confirmed by concomitant high-resolution polarized-resolved $\mu$-Raman, $\mu$-PL, and $\mu$-PL excitation ($\mu$-PLE) measurements at liquid-He temperature [21]. The strain in our monolayer samples is unintentional and is likely created during the exfoliation process. Mechanical stretching in one direction leads to uniaxial strain, which is enhanced during cooling the monolayer sample, because of the different thermal expansion coefficients of the lattices of the TMDC monolayer and the underlying SiO$_2$ substrate [21]. The distinction between strained and unstrained monolayer samples was made by using $\mu$-Raman spectroscopy measurements (see Ref. [21]). Figure 1(a) illustrates the schematics of the optical setup in a high magnetic field. For all measurements, the monolayer samples were placed inside a liquid-He bath cryostat and cooled using helium exchange gas. The measurements were performed in the backscattering configuration in a Florida-Bitter magnet generating magnetic fields up to 30 T, oriented perpendicular to the plane of the monolayer (Faraday geometry). A continuous-wave laser, emitting at 640 nm (1.93 eV), was used for excitation via a microscope objective with a numerical aperture NA = 0.55 and 40 $\times$ magnification, resulting in a laser spot of approximately 1 $\mu$m in diameter. The excitation energy was chosen to be energetically sufficiently close to the excitonic resonance, to observe a finite degree of circular and linear polarization at 0 T, but far enough to avoid resonant Raman scattering peaks.

$\mu$-PL spectra in zero magnetic field were recorded using a triple-grating spectrometer in subtractive mode (0.5 m length, 1800 grooves/mm grating) equipped with a liquid-nitrogen-cooled CCD camera. Linearly polarized $\mu$-PL measurements in high magnetic fields were performed using a single-grating spectrometer (0.3 m length) with a 1200 grooves/mm grating. The linearly polarized light for excitation and detection was selected by a half-wave plate and linear polarizer. The field-induced rotation of the linear polarization.

Faraday rotation of both the excitation and emitted light in the microscope objective was compensated by appropriate rotation of the linear polarization.

III. RESULTS

A typical $\mu$-PL spectrum of a strained WSe$_2$ monolayer sample at 4.2 K and at zero magnetic field is presented in Fig. 1(c). The highest-energy peak around 1750 meV labeled exciton corresponds to the bright neutral A-exciton transition. The feature around 1718 meV labeled trion corresponds to the negatively charged exciton. These peaks assignments are in good agreement with previously published data [11,13,22,23]. However, due to the presence of strain in our samples, both neutral exciton and trion peaks are split. To further clarify the exciton fine structure, we include in Fig. 1(c) fitted spectra obtained using bi-Lorentzian functions. In the case of the trion peak, the observed fine structure corresponds to the optically bright, negatively charged excitons—inter- and
intravalley trions. This arises from the strong e-h exchange interaction, which recently has been predicted [7,24] and observed [23,25]. In the neutral exciton case, the observed split-exciton peak arises from a combined effect of strain and electron-hole exchange [see Fig. 1(b)], where the peaks correspond to anisotropic excitons. We label these features \(X_X\) and \(X_Y\), to refer to neutral excitons along the \(x\) and \(y\) directions, respectively [21]. The corresponding energy splitting \(\Delta_0\) of about 4 meV is consistent with the extracted mechanical strain values and is in good agreement with theoretical predictions [24]. We note that the neutral exciton PL linewidth in our strained monolayer samples amounts to \(\approx 9\) meV, smaller than in unstrained samples, whose linewidth is about 12 meV. This is consistent with the effect of the weakening of the exciton-phonon coupling with increasing the uniaxial strain [19], as well as the increase of the energy separation between the indirect (\(Q\)-valley) and direct (\(K\)-valley) gaps [20], and thus provides an additional confirmation of the presence of uniaxial strain in our WSe\(_2\) monolayers.

A. Linear polarization at \(B = 0\ T\)

To gain more information about the anisotropy of the neutral exciton emission, we first characterize our sample at zero magnetic field. Figure 2(a) shows the linearly polarized PL spectra for horizontally (top panel) and vertically (bottom panel) polarized excitation of a strained WSe\(_2\) monolayer corresponding to excitation along the \(y\) and \(x\) directions. The PL emission is analyzed into its two linearly polarized components (vertical and horizontal). Three main observations are immediately apparent from the data. First, the overall neutral exciton emission partially preserves the linear polarization (valley coherence), in contrast to the trion emission, which is unpolarized (no valley coherence) in both configurations (horizontally and vertically polarized excitation) [11]. Second, the PL intensity of the neutral exciton strongly depends on the polarization orientation in excitation: In horizontally polarized excitation (labeled as \(Y\)), the horizontally polarized emission is almost two times stronger than the vertically polarized one; in vertically polarized excitation (labeled as \(X\)), the vertically polarized emission is only slightly stronger than the horizontally polarized one. Third, the overall PL emission intensity is distributed differently over the \(X_X\) and \(X_Y\) excitons, for excitation along the \(x\) and \(y\) directions. The relevant quantity in this experiment is the degree of linear polarization of the emitted light defined as DLP = \(I_4 - I_\perp)/(I_4 + I_\perp)\), where \(I_4\) (\(I_\perp\)) denotes the integrated intensity of the PL component that is parallel (perpendicular) to the excitation. Having established that the neutral exciton PL peak consists of two Lorentzian line shapes [see Fig. 2(a)], we can now extract the DLP for each anisotropic exciton in horizontally (vertically) polarized excitation. In horizontally polarized excitation, the DLP amounts to about 13% for the \(X_X\) and 39% for the \(X_Y\) exciton. In vertically polarized excitation, the DLP \(\approx 24\%\) for the \(X_X\) and 21% for the \(X_Y\) exciton. Therefore, depending on the linear polarization in excitation, the degree of linear polarization is stronger for either the \(X_X\) or \(X_Y\) exciton. In contrast to unstrained WSe\(_2\) monolayers, where the degree of linear polarization is independent on the crystal orientation and exactly follows the polarization of the optical excitation (see Jones et al. ref.[11]), in strained monolayers the DLP is dependent on linear polarization in excitation.

Collectively, these experimental results at zero field provide evidence that the polarization of the bright exciton PL emission depends on the in-plane (\(xy\)) anisotropy. At the same time, however, for the moderate strain strength (\(\approx 0.2\%\)) in our samples, both PL peaks show a finite degree of circular polarization [21]. This suggests that these two anisotropic excitons, \(X_X\) and \(X_Y\), can nevertheless preserve clear chiral optical selection rules at the \(K^\pm\) points of the Brillouin zone. A similar observation has been also reported for the monolayer (ML) MoS\(_2\) free-exciton emission under a controllable applied uniaxial tensile strain [26]. Therefore, the observed linear polarization in detection is a combination of both anisotropic and valley coherence effects. Due to the small mechanical strain in our samples, we presume that the linear polarization is mainly dominated by valley coherence which, in this case, is a result of the coherent superposition of valley states in each of the individual \(X_X\) and \(X_Y\) exciton levels.
To further characterize the linear polarization properties of $X_Y$ and $X_Y$, we measured $\mu$-PL spectra with a fixed linear polarization direction in the excitation (vertical) and detection polarization angles rotating through $180^\circ$. The raw data are presented in Fig. 2(b) as a nonpolar two-dimensional (2D) false-color plot. The exciton PL intensity changes significantly as a function of the linear polarization detection angle. Because of the small energy separation between the two exciton PL peaks, it is hard to distinguish them in this figure. However, in Fig. 2(c) we present the polar plot of the extracted emission intensity of both excitons, which clearly depends on the detection polarization angle. In agreement with previous reports [11,15], the variation of the PL intensity with the detection polarization angle shows a characteristic figure of a dipole shape dependence. The data can be well described using $I(\theta) = I_0 + I_r \cos^2(\theta + \theta_0)$, from which we extract the angle between the maximum PL intensity for each exciton. Therefore, we can observe that the principal polarization axes of the excitons are rotated by about few degrees with respect to each other.

B. Linear polarization in high magnetic fields

We now turn to the linearly polarized $\mu$-PL in high magnetic fields. These measurements have been performed under vertically polarized optical excitation. Figure 3(a) displays typical 2D false-color plots for different values of $B$, which show the PL spectra as a function of the linear polarization detection angle. The two main effects of $B$ on the linear polarization of the two excitons $X_Y$ and $X_Y$ are visible in the experimental data. First, the linearly polarized optical emission angle of the low- and high-energy exciton shifts with increasing $B$ towards a higher angle [see the maxima of the brown and green dashed lines with respect to white horizontal lines in Fig. 3(a)]. This effect is more pronounced for the $X_Y$ than the $X_Y$ exciton. Second, the degree of linear polarization is strong at low and zero $B$, but gradually reduces with increasing magnetic field, again with a behavior that is different for the $X_Y$ and $X_Y$ excitons.

These effects are clearly visible in Figs. 3(b) and 3(c) in which the same results are plotted in polar coordinates: At $B = 0$ T, the two excitons have almost the same linear polarization angle, which also coincides with the polarization direction of the excitation laser [brown arrows in Figs. 3(b) and 3(c)]. However, at $B = 20$ T the rotation of the principal polarization axis for the $X_Y$ exciton is almost two times larger than for the $X_Y$ exciton [see pink and blue symbols in Figs. 3(b) and 3(c)]. Moreover, the decrease in the DLP with increasing $B$ (decoherence effect [13,15]), which is different for the $X_Y$ and $X_Y$ exciton, is clearly observed in polar coordinates by analyzing the evolution of the polarization pattern shape. At $B = 20$ T, where the two excitons still have a finite degree of linear polarization, the $X_Y$ exciton pattern is close to a dipole, whereas the $X_Y$ pattern clearly deviates from a dipole shape.

To obtain more quantitative information about the dependence of the rotation angle on $B$ for both exciton components, we fitted their integrated PL intensities with a sinusoidal function at each magnetic field, as shown by the solid lines in Figs. 3(b) and 3(c). The results of the analysis are presented in Fig. 4(a). For the $X_Y$ exciton component, we extracted a rotation angle value of about $40^\circ$, whereas for the $X_Y$ about $23^\circ$ at the maximum field of $B = 25$ T used in our experiment. The almost twice difference in rotation angle of the two exciton components is surprising, reflecting a more complex valley decoherence mechanism. We notice that the rotation angle of the $X_Y$ exciton obtained here is comparable to the value of the neutral exciton reported in WS$_2$ monolayers [14]. In order to verify the rotation angle in WSe$_2$ monolayers without strain, we also performed control measurements under similar conditions. The complete data set is given in the Appendix, whereas the extracted rotation angle values are shown in Fig. 4(a) (purple symbols) for comparison. Indeed, in our unstrained WSe$_2$ monolayer sample we observe a very similar rotation angle of...
In strained monolayer TMDCs, applying an out-of-plane magnetic field lifts the valley degeneracy, resulting in a change in oscillation frequency of the coherent superposition of valley states by $\Delta E = \hbar \Omega_B = g \mu_B B$, where $g$ is the exciton $g$-factor and $\mu_B = 0.058 \text{ meV/T}$ is the Bohr magneton. According to Jones and Xu et al. [11], the exciton pseudospin can be illustrated on the equator of a Bloch sphere (in close analogy with the formalism used for spin). Thus, the evolution in time of the pseudospin after an initial laser light polarization along the $x$ direction is given by $|X⟩ = 1/\sqrt{2} ([K^+ e^{-\text{i} \Omega_B s / 2}] + [K^- e^{\text{i} \Omega_B s / 2}])$. As a result, after a certain time and at a finite magnetic field, the exciton pseudospin will have evolved to another position on the Bloch sphere [15]. This corresponds to a rotation of the exciton PL linear polarization considering that $\Delta E$ has a nonzero value. The extracted rotation angle as a function of magnetic field can be analyzed according to $\theta = \arctan(\Omega_B T_2^*)/2$. Here, $T_2^*$ is the fitted coherence time and can be expressed as $1/T_2^* = 1/\tau + 1/T_{d2}$, where $\tau$ is the exciton lifetime and $T_{d2}$ is the pure dephasing time, respectively.

In strained monolayer TMDCs, however, the picture becomes more complex since each of the two exciton components, being separated by $\Delta_0$ at zero magnetic field, split upon the application of an external magnetic field. Therefore, in this case we have four distinct PL lines at high fields ($X^+_K$, $X^+_X$, $X^+_Y$, and $X^+_Z$) as can be seen in the circularly polarized resolved $\mu$-PL experiment shown in Figs. 4(e) and 4(d) and schematically illustrated in Fig. 4(e). The magnetic-field-induced splitting of the two exciton components $\Delta E_x$ and $\Delta E_y$ is different and, in addition, is twice smaller than $\Delta E$ in unstrained monolayers. Therefore, we can expand the model derived by Wang et al. [15] to our strained ML considering a four-level model system (see Ref. [27] for more details). Since the rotation angle is directly proportional to the exciton $g$-factor (i.e., valley Zeeman splitting) and $T_{d2}^*$ parameter, we can define $\theta_X = \arctan(\Omega_B T_2^*)/2$ and $\theta_Y = \arctan(\Omega_B T_2^*)/2$ for each of two exciton components, where $\Omega_B (\gamma) = \Delta E_{X(\gamma)}/h = g_X(\gamma) \mu_B B / h$. The fits yield $T_{d2}^*$ values of $\pm 0.45$ and $1.97 \text{ ps}$ using the exciton $g$-factors of $g_Y \simeq -1.8 \pm 0.05$ and $g_X \simeq -2.6 \pm 0.05$, for $X_Y$ and $X_X$, respectively.
The data for the unstrained WSe$_2$ monolayer are from circularly polarized PL measurements in high magnetic fields [21]. The valley decoherence time estimated for the XX exciton is $131 \pm 0.08$ ps, which is two orders of magnitude larger than for the high-energy exciton. This is surprising since the rotation angle for the low-energy exciton is only twice larger than for the high-energy exciton and the extracted exciton $g$-factors cannot explain this large difference in their decoherence times. However, this effect might be related to the longer exciton lifetime for the higher-energy exciton. In contrast, the degree of polarization is reduced with increasing magnetic field strength up to 25 T. We find that the PL polarization degree of the experimental data using the same model as in Fig. 4(a). As expected, for both unstrained (purple) and strained (green and brown) MLs, the DLP strongly decreases with increasing magnetic field. This drop in DLP originates from the dephase induced during the exciton lifetime [13,32]. The decrease in DLP of the low-energy exciton is lower compared to the high-energy exciton, which might be attributed to the longer exciton lifetime for the higher-energy state, consistent with the observation of the larger decoherence time discussed above. However, future time-resolved PL measurements which resolve the dynamics of each exciton should provide more definitive conclusions on this matter.

In conclusion, we have measured linearly polarized PL of bright excitons in strained WSe$_2$ monolayers in an out-of-plane magnetic field up to 25 T. We find that the PL linear polarization rotation angle increases and its degree of polarization is reduced with increasing magnetic field strength for both exciton components. Interestingly, the rotation angle increase for the low-energy exciton is almost twice larger than for the high-energy exciton. In contrast, the degree of polarization has a stronger decrease for the high-energy exciton. We determine the valley coherence time constant of $T_{s2} \simeq 0.45$ and $\pm 0.08$ ps for the high- and low-energy excitons, respectively. Our results contribute to a better understanding of how strain changes the excitonic properties, provide crucial information about exciton valley coherence, and open different ways to control this effect in strained monolayer TMDCs.

![Diagram](image)

FIG. 5. (a) $\mu$-PL spectrum of an unstrained WSe$_2$ monolayer on a SiO$_2$/Si substrate measured at $T = 4.2$ K and $B = 0$ T. (b) Polar plots of extracted PL intensity for a neutral exciton in an unstrained WSe$_2$ monolayer flake at selected magnetic fields of $B = 0, 5, 10, 15, 20,$ and $25$ T. Solid lines are sinusoidal function fits to the data.

from circularly polarized PL measurements in high magnetic fields [21]. The data for the unstrained WSe$_2$ monolayer are presented in Fig. 4(a) for direct comparison. Similarly, we extract a value of $T_{s2} \simeq 0.34$ ps using an exciton $g$-factor of $-4.02 \pm 0.05$. It is interesting to note that while the $T_{s2}$ parameter is smaller in the unstrained sample, the higher values found in the strained sample are related to the smaller exciton $g$-factor values [21].

In the literature, the intrinsic exciton radiative lifetime ($\tau$) for monolayer WSe$_2$ at low temperature (4.2 K) is reported to be from 0.2 to 4 ps [28–30]. Assuming an exciton lifetime $\tau$ of 2 ps [30] in our work, we can estimate the valley decoherence time $T_{s2}$ for each of the two exciton resonances. The error here, given by both the data analysis uncertainty and the sample-to-sample variation, is less than 2 ps and leads to an uncertainty of the estimated valley decoherence time values of about $\pm 0.08$ ps. For $X_\uparrow$ we obtain a value of $T_{s2} \simeq 0.58 \pm 0.08$ ps, which is of the same order of magnitude as our derived value for the unstrained sample ($0.41 \pm 0.08$ ps) and is in very good agreement with recent theoretical predictions and experimental data [15,31]. Interestingly, the valley decoherence time estimated for the $X_\downarrow$ exciton is $131 \pm 0.08$ ps, which is two orders of magnitude larger than for the high-energy exciton. This is surprising since the rotation angle for the low-energy exciton is only twice larger than for the high-energy exciton and the extracted exciton $g$-factors cannot explain this large difference in their decoherence times. However, this effect might be related to the longer exciton lifetime for the higher-energy exciton. In contrast, the degree of polarization is reduced with increasing magnetic field strength up to 25 T. We find that the PL polarization degree of the experimental data using the same model as in Fig. 4(a). As expected, for both unstrained (purple) and strained (green and brown) MLs, the DLP strongly decreases with increasing magnetic field. This drop in DLP originates from the dephase induced during the exciton lifetime [13,32]. The decrease in DLP of the low-energy exciton is lower compared to the high-energy exciton, which might be attributed to the longer exciton lifetime for the higher-energy state, consistent with the observation of the larger decoherence time discussed above. However, future time-resolved PL measurements which resolve the dynamics of each exciton should provide more definitive conclusions on this matter.

V. CONCLUSION

In conclusion, we have measured linearly polarized PL of bright excitons in strained WSe$_2$ monolayers in an out-of-plane magnetic field up to 25 T. We find that the PL linear polarization rotation angle increases and its degree of polarization is reduced with increasing magnetic field strength for both exciton components. Interestingly, the rotation angle increase for the low-energy exciton is almost twice larger than for the high-energy exciton. In contrast, the degree of polarization has a stronger decrease for the high-energy exciton. We determine the valley coherence time constant of $T_{s2} \simeq 0.45$ and $\pm 1.97$ ps for the high- and low-energy excitons, respectively. Our results contribute to a better understanding of how strain changes the excitonic properties, provide crucial information about exciton valley coherence, and open different ways to control this effect in strained monolayer TMDCs.
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APPENDIX: ADDITIONAL DATA FROM UNSTRAINED WSe2 MONOLAYER FLAKE

As a control experiment, we measured a WSe2 monolayer flake without the presence of uniaxial strain (as determined from polarized microphotoluminescence and Raman measurements—see Ref. [21] including the Supplemental Material therein). The µ-PL spectrum of an unstrained WSe2 monolayer on a SiO2/Si substrate measured at T = 4.2 K and B = 0 T is shown in Fig. 5(a), where we also highlight the PL peak associated with the neutral exciton (X), charged exciton (T), and localized exciton (L). Following the approach we used in the main text, we systematically map the linearly polarized PL of this sample as a function of magnetic field. In Fig. 5(b) we show the extracted PL intensity for the neutral exciton in polar coordinates. The analysis of these data is discussed in the main text. These results confirm that an out-of-plane magnetic field leads to a rotation of polarization angle together with a decrease of the degree of the linear polarization, previously observed in WS2 monolayers [14].