Carrier and Polarization Dynamics in Monolayer MoS_2

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In monolayer MoS_2, optical transitions across the direct band gap are governed by chiral selection rules, allowing optical valley initialization. In time-resolved photoluminescence (PL) experiments, we find that both the polarization and emission dynamics do not change from 4 to 300 K within our time resolution. We measure a high polarization and show that under pulsed excitation the emission polarization significantly decreases with increasing laser power. We find a fast exciton emission decay time on the order of 4 ps. The absence of a clear PL polarization decay within our time resolution suggests that the initially injected polarization dominates the steady-state PL polarization. The observed decrease of the initial polarization with increasing pump photon energy hints at a possible ultrafast intervalley relaxation beyond the experimental ps time resolution. By compensating the temperature-induced change in band gap energy with the excitation laser energy, an emission polarization of 40% is recovered at 300 K, close to the maximum emission polarization for this sample at 4 K.

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Introduction.—Transition metal dichalcogenides, such as MoS_2, emerge as an exciting class of atomically flat, two-dimensional materials for electronics [1,2], optics [3], and optoelectronics [4]. In contrast to graphene, monolayer (ML) MoS_2 has a direct band gap [5,6] in the visible region of the optical spectrum. Inversion symmetry breaking (usually absent in graphene) together with the spin-orbit interaction leads to a unique coupling of carrier spin and k-space valley physics. The circular polarization (σ^+ or σ^-) of the absorbed or emitted photon can be directly associated with selective carrier excitation in one of the two nonequivalent K valleys (K_+ or K_-, respectively) [7–10], where the role of strong excitonic effects merits further investigation in this context [11–14]. The chiral optical selection rules open up very exciting possibilities of manipulating carriers in valleys with contrasting Berry phase curvatures [15], aiming for experimental manifestations of the predicted valley Hall effect [9]. Also, stable spin states have been predicted for valence and conduction states [16,17] for this material.

Up to now, optical valley initialization in ML MoS_2 is based on the analysis of the large circular polarization degree P_c of the emitted light from the direct band gap observed in continuous wave (cw) measurements following circularly polarized laser excitation [8,18–22]. An important drawback seemed to be the drastic decrease of P_c as the temperature is raised to 300 K [18–20,22]. In a simple approach, the stationary (time-integrated) polarization is determined by the initially created polarization P_0, the lifetime of the electron-hole pair τ, and the polarization decay time τ_s through $P_c = P_0/(1 + \tau/\tau_s)$ [23]. We emphasize that the polarization decay time does not correspond directly to the carrier spin flip time as in most semiconductors like GaAs [23], but it includes the scattering time between the two nonequivalent K valleys (K_+ or K_-) [9].

In this Letter, we present the first time-resolved polarization measurements in MoS_2 monolayers, providing vital information on the valley dynamics from 4 K to room temperature. We determine the key parameters that govern the stationary polarization degree P_c: Using quasiresonant excitation of the A-exciton transitions, we can infer that the photoluminescence (PL) decays within $\tau \simeq 4$ ps. For pulsed laser excitation, we observe a decrease of P_c with increasing laser power. We show that the PL polarization remains nearly constant in time for experiments from 4 up to 300 K, a necessary condition for the success of future valley Hall effect experiments based on optically initialized k-valley polarization [9]. In addition, τ does not vary significantly over this temperature range. These results are surprising when considering the reported decrease of P_c in cw experiments when going from 4 to 300 K reported in the literature [18–20,22]. By tuning the laser following the shift of the A-exciton resonance with the temperature, we are able to recover at room temperature ~80% of the polarization observed at 4 K in our sample. The absence of a clear PL polarization decay within our time resolution suggests that the initially injected polarization P_0, which dominates the steady state PL polarization, is responsible for this observation.

Samples and setup.—MoS_2 flakes are obtained by micromechanical cleavage of a natural bulk MoS_2 crystal [24] (from SPI Supplies, USA) on a Si/90 nm SiO_2 substrate. The 1 ML region is identified by optical contrast and very clearly in PL spectroscopy [5]. Experiments between $T = 4$ and 300 K are carried out in a confocal microscope optimized for polarized PL experiments [25]. The MoS_2 flake is excited by picosecond pulses generated by a tunable frequency-doubled optical parametric oscillator synchronously pumped by a mode-locked Ti:Sa laser. The typical pulse and spectral width are 1.6 ps and 3 meV, respectively; the repetition rate is 80 MHz. The laser wavelength can be tuned between 500 and 740 nm. The detection spot diameter is ≈ 1 μm. For time-integrated experiments, the PL emission is dispersed in a spectrometer and detected with a Si-CCD camera. For time-resolved experiments, the PL signal is dispersed by an imaging spectrometer and detected by a synchroscan Hamamatsu streak camera with an overall time resolution of 4 ps. The PL polarization P_c defined as $P_c = (I_{\sigma+} - I_{\sigma-})/(I_{\sigma+} + I_{\sigma-})$ is analyzed by a quarter-wave plate placed in front of a linear polarizer. Here, $I_{\sigma+}(I_{\sigma-})$ denotes the intensity of the right (σ^+) and left (σ^-) circularly polarized emission.

Experimental results.—Figure 1(a) displays the total photoluminescence intensity dynamics at $T = 4$ K following a σ^+ polarized picosecond excitation laser pulse with an energy $E_{\mathrm{Laser}} = 1.965$ eV, which is within the broad A-exciton absorption line [13,18]. The detection energy corresponds to the PL peak energy $E_{\mathrm{Det}} = 1.867$ eV. The average laser power used for all experiments in Figs. 1–3 is below 1 mW/μm^2, well below the absorption saturation and in the absence of sample heating effects, as discussed in detail in the Supplemental Material [26]. We do not observe any variation of the dynamics when the detection energy is varied within the A-exciton spectrum [27]. Though the MoS_2 PL dynamics is very fast, we see in Fig. 1 that it occurs on a slightly longer time scale compared to the one defined by the temporal resolution of the setup [compare the MoS_2 PL and laser pulse detection in Fig. 1(a)]. Using a deconvolution based on Gaussian functions, we can infer that the MoS_2 emission time is about 4.5 ps. We emphasize that this fast PL dynamics is obtained in excitation conditions where exclusively the A exciton (not B) in the K_+ valley is excited [see inset of Fig. 1(a)]. Here the energy difference between excitation and detection $E_{\mathrm{Laser}} - E_{\mathrm{Det}}$ is about 100 meV. Similarly fast dynamics were recorded in strongly nonresonant excitation conditions with $E_{\mathrm{Laser}} - E_{\mathrm{Det}} > 1$ eV [28,29].

In Fig. 1(b), the right ($I_{\sigma+}$) and left ($I_{\sigma-}$) circularly polarized luminescence components have been detected using a σ^+ polarized laser (measured $P_c^{\mathrm{Laser}} > 99\%$). Remarkably, the PL circular polarization degree is large and remains almost constant during the short exciton emission, around 50% for a laser excitation power $P_{\mathrm{Laser}} \simeq 550$ μW/μm^2 [blue curve in Fig. 1(b)]. Lowering the excitation power by 2 orders of magnitude has a strong impact: The polarization still remains nearly constant but at a higher value of 60% [green curve in Fig. 1(b)]. As $P_0 < P_c^{\mathrm{Laser}}$, either the polarization generation at this laser energy is not 100% efficient (due to the optical selection rules), or there exists an ultrafast initial polarization decay due to intervalley relaxation much shorter than 1 ps that we do not resolve. Because of the sequential recording of σ^+ and σ^- polarized kinetics, there is an experimental uncertainty of $\Delta t \sim 0.7$ ps when fixing the time origin of the σ^+ emission with respect to σ^-. This results in an experimental

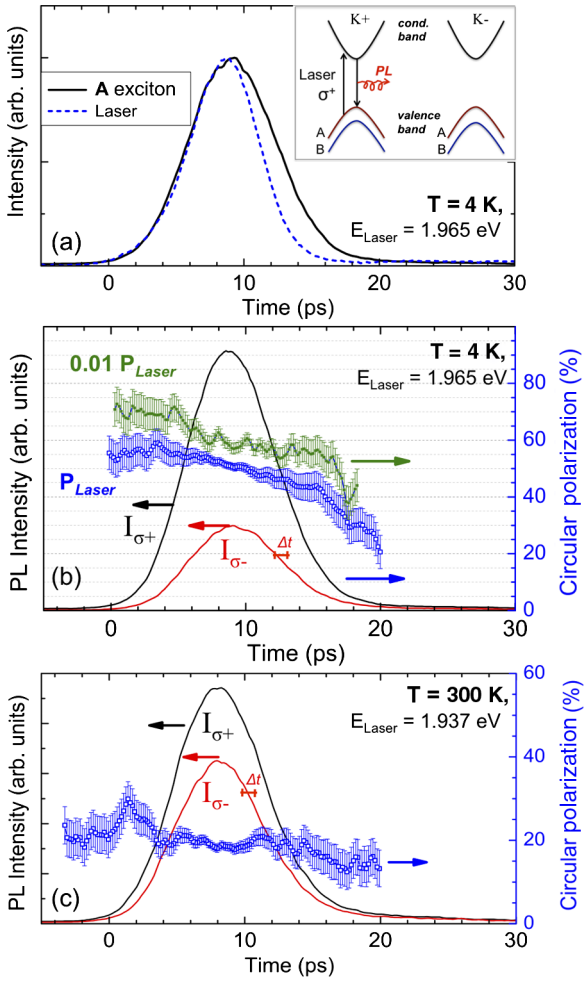

FIG. 1 (color online). The time-resolved photoluminescence of an A exciton. (a) Laser pulse (blue line) and PL emission (black line) intensity at $T = 4$ K detected at the maximum of an A-exciton PL $E_{\mathrm{Det}} = 1.867$ eV as a function of time. Inset: Chiral optical selection rules in 1 ML MoS_2 (b) $T = 4$ K, $E_{\mathrm{Laser}} = 1.965$ eV, $E_{\mathrm{Det}} = 1.867$ eV. Laser polarization σ^+. Left axis: σ^+ (σ^-) polarized PL emission intensity presented in black (red) as a function of time. Right axis: Circular polarization degree during exciton emission (blue hollow squares: excitation power $P_{\mathrm{Laser}} \simeq 550$ μW/μm^2; green full squares: 0.01 P_{Laser}), error bars take into account the uncertainty in time origin $\Delta t \sim 0.7$ ps. (c) Same as (b) but for $T = 300$ K, $E_{\mathrm{Laser}} = 1.937$ eV, $E_{\mathrm{Det}} = 1.828$ eV.

uncertainty when determining the circular PL polarization, as indicated by the error bars in Fig. 1(b). As a result of this time jitter and the short exciton emission time, our experiments do not allow an accurate determination of the spin or valley relaxation time τ_s. The emission at room temperature is very similar to 4 K with $\tau \sim 4.5$ ps. Figure 1(c) shows $P_c \simeq 20\%$ constant in time for a laser excitation energy $E_{\mathrm{Laser}} = 1.937$ eV. The dependence of P_c as a function of the excitation laser energy will be discussed below. Remarkably, the PL circular polarization degree, which probes the valley initialization measured in the time-resolved experiment, is similar to the one obtained in cw experiments as a result of the very short exciton lifetime and the absence of measurable polarization decay within this short emission time.

In Fig. 2(a), we show that when raising the temperature, in addition to the ps exciton decay, a longer-lived component is observed. This is similar to the findings of Korn *et al.* [28] under highly nonresonant excitation. This measured long-lived PL component is essentially unpolarized in Fig. 2(a), and the intensity is very weak compared to the short main PL emission (log scale). Therefore, even at room temperature, the short component, see Fig. 1(c), determines P_c. In addition to the main A exciton, localized excitons emitting at lower energy ($E_{\mathrm{Det}} = 1.775$ eV) are observed [18,20,28], see the inset of Fig. 2(a). The localized exciton emission decays within about 125 ps at $T = 4$ K [see Fig. 2(b)] and is not detectable at a higher temperature. The polarization dynamics is shown in the inset of Fig. 2(b): As the A-exciton and the broad localized exciton emissions spectrally slightly overlap, we detect the remaining A-exciton polarization at short times before detecting the essentially unpolarized emission of the localized excitons. It is important to note that the localized exciton polarization dynamics is expected to be more sensitive to the sample parameters (substrate material, interface defects, etc.) than the A-exciton emission.

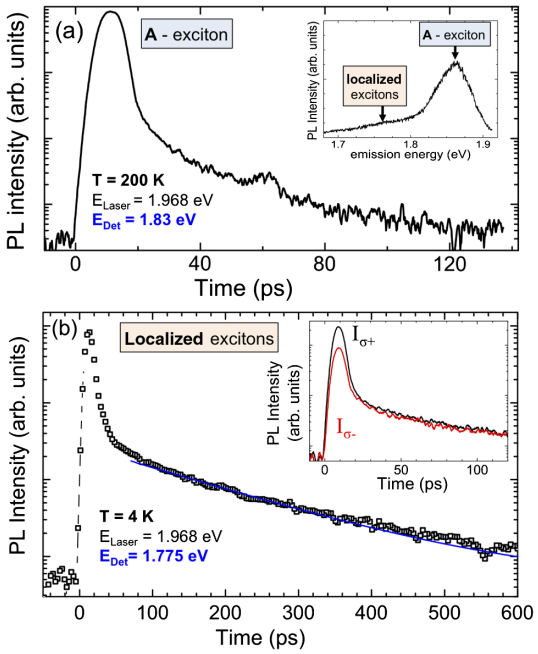

FIG. 2 (color online). The time-resolved photoluminescence (a) $T = 200$ K, $E_{\mathrm{Laser}} = 1.968$ eV, $E_{\mathrm{Det}} = 1.83$ eV. A-exciton PL intensity as a function of time plotted in log scale to emphasize the weak slow component that appears when raising T. The small peak at about 50 ps is due to a laser reflection in the setup. Inset: cw-PL spectrum at $T = 4$ K showing the energy of the intrinsic A-exciton emission and localized exciton emission. (b) $T = 4$ K, $E_{\mathrm{Laser}} = 1.968$ eV, $E_{\mathrm{Det}} = 1.775$ eV. The localized exciton PL intensity as a function of time (black). Blue line: Fit with a single exponential decay ($\tau_{loc} \simeq 125$ ps). Inset: The polarization-resolved emission of an A exciton and localized exciton which spectrally slightly overlap.

The time-resolved measurements in Fig. 1(c) show a nearly constant polarization during the exciton PL emission at $T = 300$ K. Yet in the literature, the time-integrated polarization of the A-exciton PL at room temperature is reported to be considerably lower than at 4 K [18,20,22]. We confirm these observations in our sample, see the Supplemental Material [26]. Here, it is important to take into account the considerable redshift of the direct band gap as the temperature increases [28]. We have, therefore, performed time- and polarization-resolved photoluminescence excitation (PLE) experiments, see Fig. 3, to vary the initially generated polarization P_0. The time-integrated PL is detected at its peak energy (1.867 and 1.828 eV at $T = 4$ and 300 K, respectively). As already observed by different groups [18–21], the PL circular polarization degree and, thus, the valley initialization decrease at $T = 4$ K [Fig. 3(a)] when the laser excitation energy increases: It varies for the sample investigated here from $P_c \simeq 50\%$ for $E_{\mathrm{Laser}} = 1.958$ eV down to a value close to zero for $E_{\mathrm{Laser}} = 2.06$ eV, similar to the findings by Kioseoglou *et al.* [21]. Here we observe that P_c slightly increases again up to $P_c \simeq 10\%$ for $E_{\mathrm{Laser}} = 2.2$ eV. Though the polarization minimum is observed roughly in the region where the B exciton is photogenerated (see the vertical dotted line), its origin needs further clarification since the B exciton absorbs and emits the same light helicity as the A exciton in a given K valley [8,9]. The energetically close lying indirect transition from the Γ valley valence band to the conduction band, which is unpolarized, could play a role [30,31]. When comparing the results obtained on different samples in the literature [18–22], it is important to take into account the laser excitation (power, pulsed, or cw) and the exact form of the emission spectrum [26].

A key result is presented in Fig. 3(b). We perform the same PLE experiments as in Fig. 3(a) but at room temperature. When the laser is far from resonance, we observe close to zero polarization. Remarkably, as we lower the laser energy and become more and more resonant, the polarization drastically increases in the same manner as at 4 K. For the closest energy to resonance that was achievable

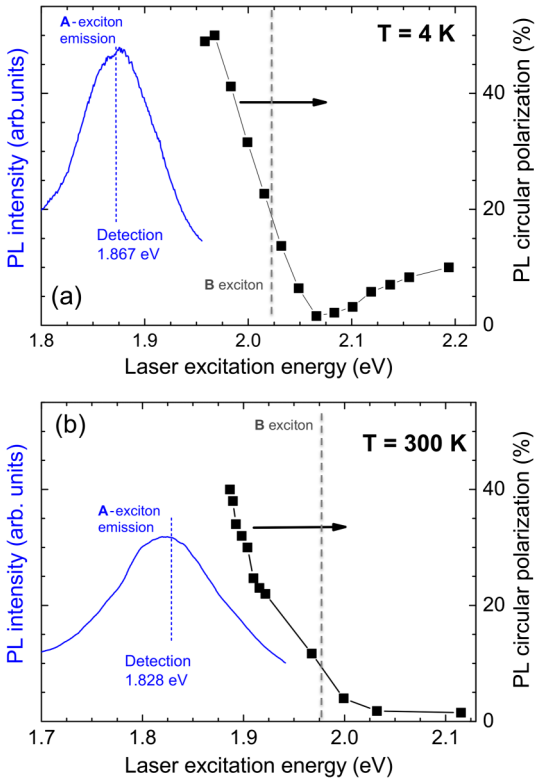

FIG. 3 (color online). The PL polarization as a function of laser excitation energy (a) $T = 4$ K, $P_{\mathrm{Laser}} \simeq 550\ \mu\mathrm{W}/\mu\mathrm{m}^2$ detected on the A-exciton PL maximum $E_{\mathrm{Det}} = 1.867$ eV. The A-exciton emission (blue) is shown. (b) Same as (a) but for $T = 300$ K, $P_{\mathrm{Laser}} \simeq 950\ \mu\mathrm{W}/\mu\mathrm{m}^2$, $E_{\mathrm{Det}} = 1.828$ eV.

in practice with our setup (filter cutoff for stray laser light), we measure an emission polarization of $P_c(300\ \mathrm{K}) = 40\%$, close to the maximum observed at 4 K of $P_c(4\ \mathrm{K}) = 50\%$ [32]. This is very encouraging, as the optical initialization of valley polarization with a suitable excitation source can, therefore, be very efficient even at room temperature. Here it would be extremely useful to investigate how the strong Coulomb interaction [11–14] influences the polarization at 300 K.

Discussion.—The few time-resolved measurements reported in the literature for 1 ML MoS_2 use highly nonresonant excitation and did not analyze the polarization of the emission [28,29,33]. In Refs. [18,29], the authors suggest that nonradiative recombination of the excitons could explain the first short decay observed from 4 to 300 K. We can infer from our time- and polarization-resolved measurements that the detected polarization in time-integrated experiments is due to the emission during this short time window. If this initial decay is, indeed, limited by nonradiative processes or an intrinsic exciton lifetime is still an open question. The exciton binding energy is estimated to be in the hundreds of meV range [11,12,14]. Systems with large exciton binding energies, such as organic films and carbon nanotubes, have intrinsic exciton radiative lifetimes on the order of a few ps [34–36]. In our measurements, the PL decay time τ does not change with the temperature within our time resolution; we do not observe any activation or any other typical signature of nonradiative processes. For comparison, for high-quality GaAs quantum well structures, the free Wannier-exciton radiative recombination time increases with the temperature [37].

An argument in favor of a radiative exciton decay within a few ps comes from the observation of the B-exciton emission, 150 meV higher in energy than the A exciton [18,20], as the radiative recombination of the B exciton is in competition with nonradiative decay and relaxation to the A exciton. Here a theoretical prediction of the intrinsic exciton recombination is needed to guide future experiments in this promising system.

Also, in the future, the influence of the substrate on the polarization dynamics needs to be investigated. Here we used MoS_2 MLs on SiO_2, the most practical substrate for (opto)electronic devices. Although time-resolved experiments on suspended MoS_2 MLs gave similar time-resolved absorption results to the experiments using substrates [29], a comparison with MoS_2 on boron nitride where the localized exciton emission was suppressed [13,18] would be important to clarify the nature of the observed PL emission.

The very fast exciton decay time measured here in MoS_2 MLs could help explain several key observations: (i) application of a transverse magnetic field will only show an influence on the polarization of the ML PL if the precession time is shorter than 4 ps [20] and (ii) coherence between valley excitons probed through the observation of stationary linearly polarized luminescence in related WSe_2 devices, which are expected to have similar physical properties [38].

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