Resonance profiles of valley polarization in single-layer MoS$_2$ and MoSe$_2$

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In this work we present photoluminescence measurements with different excitation energies on single-layer MoS$_2$ and MoSe$_2$ in order to examine the resonance behavior of the conservation of circular polarization in these TMDCs. We find that the circular polarization of the emitted light is conserved to 100 % in MoS$_2$ and 84 %/79 % ($A/A^-$ peaks) in MoSe$_2$ close to resonance. The values for MoSe$_2$ surpass any previously reported value. However, in contrast to previous predictions, the degree of circular polarization decreases clearly at energies less than the 2 LA phonon energy above the resonance.

Our findings indicate that at least two competing processes underly the depolarization of the emission in single-layer transition metal dichalcogenides.

Transition metal dichalcogenides (TMDCs) like MoS$_2$ and MoSe$_2$ have emerged as promising materials for various future applications due to their properties when thinned down to a single layer (SL). In the SL limit, they become direct semiconductors with their band gaps located at the $K$ points in the Brillouin zone (cf. Fig. 1a). Strong spin-orbit coupling results in a large valence band splitting of a few hundred meV at the $K$ points; the conduction bands are split by a few meV. This splitting causes the so-called $A$ and $B$ exciton transitions (Fig. 1b). Optical selection rules for circularly polarized light in single layers lead to transitions where electrons and holes are exclusively generated at either $K$ or $K'$, as time reversal symmetry and absence of inversion symmetry couple pseudospin and valley (so-called valley polarization). Hence, excitation with circularly polarized light is followed by emission of a photon with the same circular polarization. However, since the first published experimental evidence of valley polarization in 2012 [1, 2], most groups find non-perfect polarization in different experimental conditions [2–4]. The origin of such reduced circular polarization of the emitted light from these materials is, however, still controversially discussed. Different approaches of how the conservation of circular polarization is limited are suggested in the literature. Two of these mechanisms are based on the formation of an exciton in the respective other $K$ point. The first, often called ”2LA mechanism”, is a two-phonon (LA: longitudinal acoustic) assisted scattering of the exciton [5–7]. The second process generates an exciton at $K'$ ($K$) while destroying the photoexcited exciton at $K$ ($K'$) by interference of the exciton wavefunctions [8][10]. We will refer to this process as the valley exchange mechanism.

One of the reasons for the diverse speculations on the depolarization mechanism is certainly the lack of data with excitation close to the emission lines, in particular from within the energy range of up to the energy of two LA phonons above the emission energy.

In this letter we present circularly polarized photoluminescence excitation (PLE) measurements of MoS$_2$ and MoSe$_2$ close to the resonance of their exciton and trion emissions. We were able to record spectra less than 10 meV away from the excitation energy by using a triple monochromator setup and thereby overcoming the technical restrictions of previously published results. We find that the emitted circular polarized light is conserved to 100 % in MoS$_2$ and 84 %/79 % ($A/A^-$ peaks) in MoSe$_2$
when exciting close to the resonance. However, in our experiments the decrease of the degree of polarization starts at lower excess energy than the previously predicted 2 LA transition, the contrast-like degree of circular polarization is introduced, with $I_{\sigma^+}$ ($I_{\sigma^-}$) being the photoluminescence (PL) emission intensity of the $\sigma^+$ ($\sigma^-$) circular polarization. Accordingly, full conservation of $\sigma^+$ excitation is reflected in a degree of $\rho = 1$, while equal intensities of $\sigma^+$ and $\sigma^-$ polarizations result in a degree of $\rho = 0$.

For MoS$_2$ we observe full conservation of polarization in the case of resonant excitation (Fig. 2). For MoSe$_2$, however, this is not observed (Fig. 2). The maximum DOP $\rho$ is only about 84% (79%) for the $A$ ($A^-$) emission, which are still the highest values reported so far for MoSe$_2$.

In figure 3, we plot the resonance behavior of the circular polarization $\rho$. When increasing the excitation energy, thus providing excess energy $\Delta E$ to the system, we observe a short plateau with full conservation ($\rho = 1$) in the case of MoS$_2$. The energy range of the plateau is sample dependent (cf. Fig. 3). With further increasing excess energy, a decline of the DOP is observed. For MoSe$_2$ no plateau, but only the decline of polarization for rising excess energies $\Delta E$ is found (see Fig. 3).

In previous studies performed by Kioseoglou et al., a similar behavior was observed (cf. Fig. 4). With the Kioseoglou model, the excitons are scattered between the $K$ and $K'$ points by simultaneous scattering of electron
and hole by two LA (longitudinal acoustic) phonons. In their model, scattering is only possible if sufficient energy is provided to emit the two LA phonons. These two phonons are phonons from the $K$ point, i.e., phonons with a wave vector $\overrightarrow{IK}$ (cf. Fig. 1). However, the phonon dispersions of MoS$_2$ and MoSe$_2$ are not experimentally known at the $K$ point. Therefore, the phonon energy can only be estimated from second-order Raman scattering [10] or taken from calculations [17]. Following these estimations, the energy of the 2 LA phonons in MoS$_2$ (MoSe$_2$) at the $K$ point is around 60 meV [17] (39 meV [18]). In our measurements of MoS$_2$, on the other hand, the decrease of the DOP $\rho$ starts already well below 60 meV excess energy (Fig. 4a). For MoSe$_2$, no full conservation of polarization can be observed at all. Note that the measurement on MoSe$_2$ closest to resonance was performed with an excess energy of 3 meV, well below the energy of two LA phonons (Fig. 4b).

In MoS$_2$, the decline of the DOP $\rho$ is sample dependent, as different samples of MoS$_2$ exhibit different trends (series 1 and 2 in figure 4a). The crystal quality of our samples and those used in the experiments performed by Kioseoglou et al. [7] should be comparable, as the preparation procedure was the same. However, we expect that environmental effects, in particular surface adsorbates, have influenced the flake used for series 1 in figure 4a). The measurements were taken 10 months after exfoliation; other experiments with low laser power and in cryogenic environment had been performed before. During this period the flake was stored in ambient conditions.

In contrast, the flake for series 2 was put in vacuum and was directly measured after exfoliation.

Furthermore, the observed localized exciton peak L at 1.803 eV might hint at exciton scattering on defects. These could support the scattering between the $K$ valleys. Depending on the type of defect, it could, e.g., provide the necessary amount of momentum for an electron (hole) to scatter to the respective other $K$ valley, reducing the required excess energy to one LA($K$) phonon equivalent. On the other hand, Mak et al. [4] have also observed a “trapped exciton” feature around 1.8 eV and still achieved full conservation of circular polarization with approximately 60 meV excess energy.

Another approach attributed the decline in the DOP $\rho$ with rising excess energy to the valley exchange mechanism [10]. The PLE measurements of Ref. [10] for MoSe$_2$ are shown in Fig. 4b) for comparison (green stars). The authors present a rate equation model, where in steady-state conditions the maximum DOP $\rho$ is depending on the times of excitonic recombination, scattering between the bright and dark states within the valley, and the valley exchange [10]. From these they conclude a maximum possible polarization of about 35% in MoSe$_2$. In our measurements, however, we find a higher degree of polarization.

According to the Maiale-Silva-Sham mechanism [19], underlying the valley exchange, the exchange efficiency is proportional to the exciton center-of-mass momentum and therefore dependent on the excess energy. Assuming parabolic bands, the dependence of the conserva-
tion of polarization translates into a proportionality of \( \rho \propto 1/\sqrt{\Delta E} \). This relation is fitted to our measurements of MoSe\(_2\) (cf. fig 4b, dashed line) and is in good agreement with our data and the values acquired by Baranowski et al.\(^{10}\), however deviates from those of Ref.\(^{7}\).

As the assumption of parabolic bands is only valid close to the band extrema, it is reasonable that the fit does not describe the trend at higher excess energies. Intriguingly this dependence does not describe the acquired polarization values of MoS\(_2\). We suggest that the difference might be attributed to different intrinsic properties of the materials. The interplay of different exciton- or electron-phonon coupling and exchange constants as well as lifetimes, and the availability of scattering or relaxation channels could lead to a different dominant depolarization mechanism.

To conclude, we have presented PLE measurements of circularly polarized light emission from MoS\(_2\) and MoSe\(_2\). We observe a high degree of conservation of circular polarization when exciting close to the resonance with the optical transition. However, the DOP \( \rho \) is reduced as soon as the resonance condition is left. For MoSe\(_2\), we observe a degree of polarization \( \rho \) of 84\% (79\%) for the A exciton (trion) emission, which are the highest reported values for MoSe\(_2\), to the best of our knowledge. We find that the nature of the generation and valley depolarization of excitons in TMDCs is so far not fully understood, as none of the proposed mechanisms can describe the DOP in TMDCs in the vicinity of the resonances. However, the trends of the DOP of MoS\(_2\) and MoSe\(_2\) are partly in agreement with the two described models stemming from the 2LA mechanism and the valley exchange, respectively. This is suggesting that more than one mechanism is reducing the DOP in different TMDCs. Further investigations, especially of the electron and hole scattering involving phonons, are needed for better understanding of the processes relevant for valleytronics.

**METHODS**

*Sample preparation.* Single-layer samples were exfoliated by mechanical cleavage onto silicon with a top layer of 90 nm silicon oxide, yielding flakes of \( \approx 10 \mu m \) size. Single-layer flakes were identified by RGB-contrast measurements with an optical microscope\(^{20}\) and verified by the absence of the indirect gap transition (MoS\(_2\)) or of the \( A_{1g}/A_{1g}^/B_{2g} \) few-layer/bulk Raman mode\(^{11}\) (MoSe\(_2\)).

*Optical measurements.* Micro-photoluminescence spectra in backscattering geometry were acquired using a Dilor XY800 triple monochromator setup equipped with a liquid nitrogen cooled CCD. For continuous wave excitation Rhodamine 6G (LC5900) and DCM special (LC6501) dye lasers as well as a Ti:Sapphire laser were used, enabling continuously tunable excitation from 575 nm to >800 nm (2.16 \ldots <1.55 eV). The lasers were guided through a linear polarization filter before entering the microscope. Circular polarization was achieved by using an achromatic quarter-wave plate mounted just above the objective lens to avoid optics-induced distortions. The emitted circularly polarized luminescence was changed to linear polarization with the same quarter-wave plate, while selection of the respective polarization was performed by a linear analyzer. The power density on the sample was always kept below \( 10^6 \) W/m\(^2\) (300 \( \mu \)W on a 2 \( \mu \)m laser spot) to avoid damage and excessive heating.

The samples were cooled to 20 K by using a helium cooled cold-finger micro cryostat. The sample temperature was kept at cryogenic temperatures to avoid temperature-cycle induced changes from, e.g., changing dielectric environment due to absorbed water, damage induced by freezing adsorbates, etc.

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