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Robust optical emission polarization in MoS_2 monolayers through selective valley excitation

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We report polarization resolved photoluminescence from monolayer MoS_2, a two-dimensional, noncentrosymmetric crystal with direct energy gaps at two different valleys in momentum space. The inherent chiral optical selectivity allows exciting one of these valleys, and close to 90% polarized emission at 4 K is observed with 40% polarization remaining at 300 K. The high polarization degree of the emission remains unchanged in transverse magnetic fields up to 9 T indicating robust, selective valley excitation.

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Introduction. The spectacular progress in controlling the electronic properties of graphene[1,2] has triggered research in alternative atomically thin two-dimensional crystals. Here monolayer (ML) MoS_2 [see the structure in the inset of Fig. 3(a)] has emerged as a very promising material for optical and spin applications for mainly two reasons. First, the indirect bulk semiconductor MoS_2 becomes direct when thinned to 1 ML,[3–5] resulting in efficient optical absorption and emission[3–6] and promising reports on using ML MoS_2 as an active field effect transistor (FET) channel.[7] Second, inversion symmetry breaking (usually absent in graphene) together with the spin-orbit interaction leads to a coupling of carrier spin and k-space valley physics, i.e., 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). This chiral optical valley selectivity has been theoretically predicted[8–10] with very recent encouraging experimental results reporting indeed strong polarization of the photoluminescence (PL) emission in ML MoS_2.[9,11,12]

The selection rules for the direct, dipole allowed optical transitions in a MoS_2 ML are represented in Fig. 2(a). The conduction band (CB) minimum located at the K_- and K_+ points is spin degenerate.[13] In contrast, at the valence band (VB) maximum, also located at the $K_\pm$ points, spin-orbit coupling induces a splitting between spin up and spin down bands of about 150 meV due to the absence of inversion symmetry in *monolayer* MoS_2.[8] Therefore at low temperatures a spin flip to the opposite spin state within the same valley is energetically forbidden, i.e., a flip between VBs ***A*** and ***B***—see Fig. 2(a).[11] Another striking feature is the reversed order of valence electron spin up and down states when going from the K_- to K_+ valley. So to change its spin state, the valence carrier has to (i) change valley, i.e., compensate a change in wave vector comparable to the size of the Brillouin zone, and (ii) in addition change its orbital angular momentum [see Fig. 2(a)]. As a result, a change in valence carrier spin state and hence valley in k space will be far less likely in a MoS_2 ML than the common spin flip mechanisms evoked in well studied semiconductors such as GaAs,[14] making ML MoS_2 a promising system for the development of photoinduced spin Hall and valley Hall experiments. Several original experimental schemes propose to use a stable valley index in analogy to the electron charge or spin as an information carrier in AlAs (Ref. 15) and graphene samples with deliberately broken inversion symmetry.[16–18] The simple valley initialization via polarized laser excitation makes ML MoS_2 an extremely promising system for valleytronics, and investigating the robustness of the valley degree of freedom is of key importance for a practical implementation. Our approach is to trace the change of valley index experimentally via the photon emission, which would have the opposite polarization compared to the excitation laser.[19] The robustness of the optically created polarization is confirmed in strong transverse magnetic fields and at temperatures up to 300 K. Our experimental work allows to further test the association of the high PL emission polarization with selective valley excitation.

Samples and setup. MoS_2 flakes are obtained by micromechanical cleavage of a natural bulk MoS_2 crystal[20](from SPI Supplies, USA) on a Si/90 nm SiO_2 substrate. The ML region is identified by optical contrast and very clearly in PL spectroscopy, based on the fact that MoS_2 becomes a direct seminconductor only for a thickness <2 ML. Experiments on the same sample as in Ref. 9 are carried out in a home-built confocal microscope optimized for polarized PL experiments[21] in an attoDry magnetocryostat. The detection spot diameter is ≈ 1 μm, optical excitation is achieved with a HeNe laser (1.96 eV, typical power 50 μW) that is for $T < 50$ K close the resonance with the lowest energy, direct transition [red transition K_+ valley in Fig. 2(a)], and the resulting emission polarization is analyzed in the circular basis, dispersed in a spectrometer, and detected with an Si-CCD camera. For higher energy excitation a frequency doubled Nd:YAG laser at 2.33 eV is used [as in Fig. 2(b)]. The sample temperature can be controlled between 4 and 300 K, and a transverse magnetic field B_T up to 9 T in the plane of the MoS_2 monolayer (Voigt geometry) is applied—see the inset of Fig. 3(a).

Experimental results. First we investigate the temperature dependence of the PL polarization, monitoring if the optically created carriers can change valley in k space, for example, through scattering with phonons of suitable wave vector. Before discussing polarization, we note that the overall spectral and temperature dependence of the PL emission is very similar to Ref. 6 where the same substrate was used: Independent of

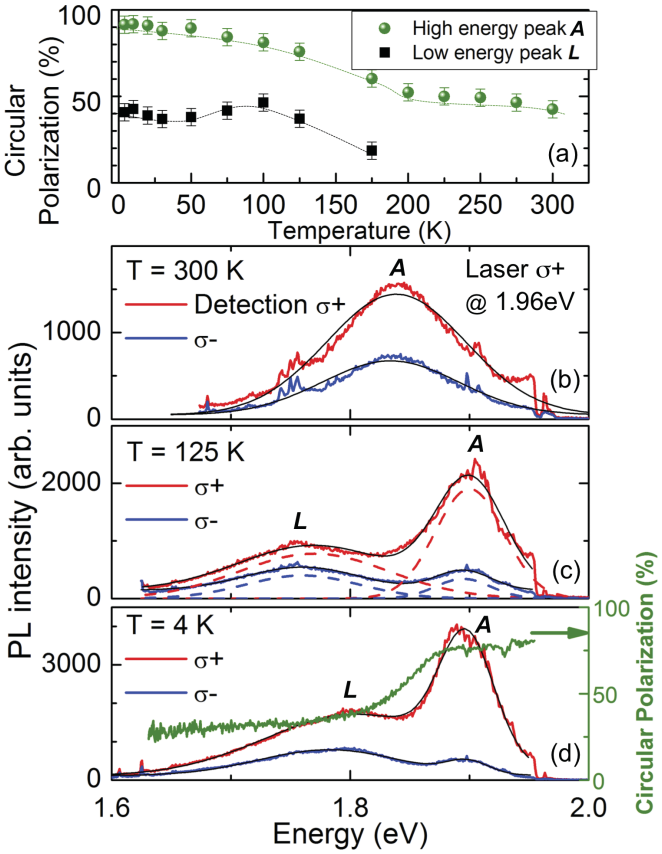

FIG. 1. (Color online) (a) Measured PL circular polarization degree of a 1 ML MoS_2 as a function of temperature. Low energy peak (***L***) not detectable for $T > 175$ K. Dotted lines are a guide to the eye. (b) PL spectra copolarized (red/light gray) and cross polarized (blue/dark gray) with respect to the σ^+ polarized excitation laser (HeNe at 1.96 eV). At 300 K only the high energy peak ***A*** is detectable. Black curves indicate fit to the data with Gaussians. (c) Same as (b) but at $T = 125$ K. Both ***L*** and ***A*** peaks are detectable and the polarization degree is extracted by fitting them separately (dashed lines). (d) Same as (c) but at $T = 4$ K; the (green) right axis shows the circular polarization. PL intensity drops as a function of temperature; counts in (b)–(d) are normalized for better visibility.

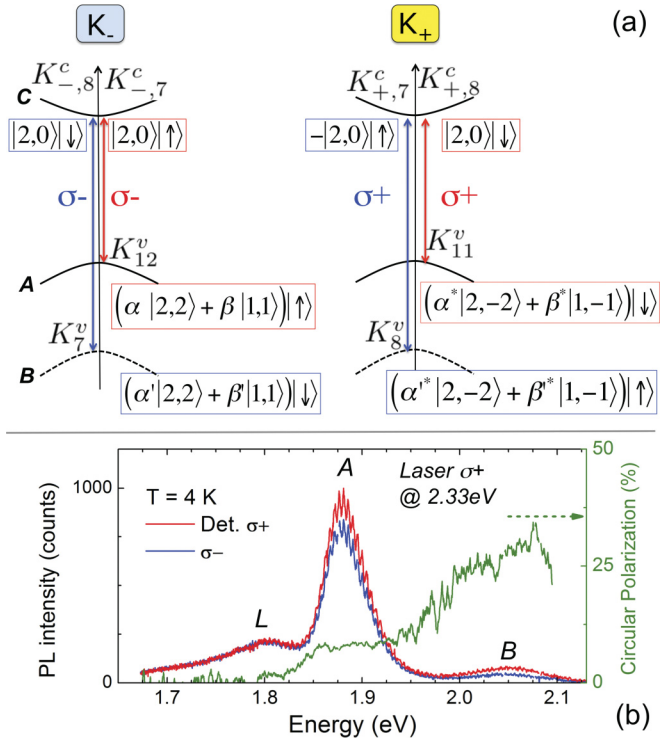

FIG. 2. (Color online) (a) Selection rules for optical dipole transitions in a simple single particle picture in K_+ and K_- valleys at zero magnetic field, adapted from Refs. 8–10; states are represented as $|L,M\rangle$ for valence states, and $|\uparrow\rangle$ ($|\downarrow\rangle$) stand for electron spin up (down). For simplicity, the k-linear term in the CB is neglected, and the ***A***(***B***) VBs for K_+ and K_- are degenerate in energy. Local trigonal symmetry of electron states at $K_\pm$ points is C_{3h} in Koster notation (Ref. 24), with states labeled using corresponding group representations (b). PL spectra at $T = 4$ K copolarized (red/light gray) and cross polarized (blue/dark gray) with respect to the σ^+ polarized highly nonresonant excitation laser at 2.33 eV. Transitions ***L*** and ***A*** are visible in addition to the ***B*** exciton. The small periodic signal variations are due to optical interference in the setup. The (green) right axis shows the PL circular polarization.

the laser excitation power, we observe a low energy peak ***L*** centered at 4 K close to 1.8 eV, which is only detectable for $T < 175$ K. The exact origin of peak ***L***, most likely linked to bound exciton states,[6] is still under investigation. The emission intensity of peak ***L*** has been found to depend on the substrate material used, SiO_2 or BN,[11] and can be strongly reduced through oxide coverage.[22] The remainder of the discussion is devoted to the high energy peak ***A*** observed from 4 K (centered at ≈1.9 eV) to room temperature which is attributed to the free exciton emission, expected to obey the selection rules presented in Fig. 2(a).

We can separately access the polarization properties of the two dominant peaks ***A*** and ***L*** of the emission by fitting two Gaussians as in Fig. 1(c). Following excitation with a circularly σ^+ polarized HeNe laser we observe at $T = 4$ K a strongly circularly σ^+ polarized emission, confirming very recent reports.[9,11,12] Here the polarization of the free exciton peak ***A*** is about 90% [see Fig. 1(b)], close to the theoretically predicted 100% for the direct transition. When raising the temperature no measurable change occurs for the ***A*** line polarization up to about $T = 50$ K, but beyond this temperature a steady decrease of the emitted polarization is observed. At room temperature, a substantial polarization of 40% remains, as demonstrated in Fig. 1(c), indicating that selective optical k-valley excitation with a polarized laser is still possible.

Figure 2(b) presents the σ^+ and σ^- circularly polarized PL intensity and the corresponding circular polarization following highly nonresonant excitation at 2.33 eV. In this case both ***A*** (as observed in Fig. 1) and ***B*** VB to CB transitions are possible, and we observe indeed hot luminescence from the CB to ***B*** band transition, which is polarized up to about 30%. At this high laser energy the valley selectivity is not very high as the ground state transition A is only about 10% polarized. The distance in energy between ***A*** and ***B*** bands is ≈170 meV, in good agreement with the predicted 150 meV.[10] Based on the predicted, strict valley selectivity, hot luminescence from the CB to ***B*** transition is polarized dominantly σ^+,

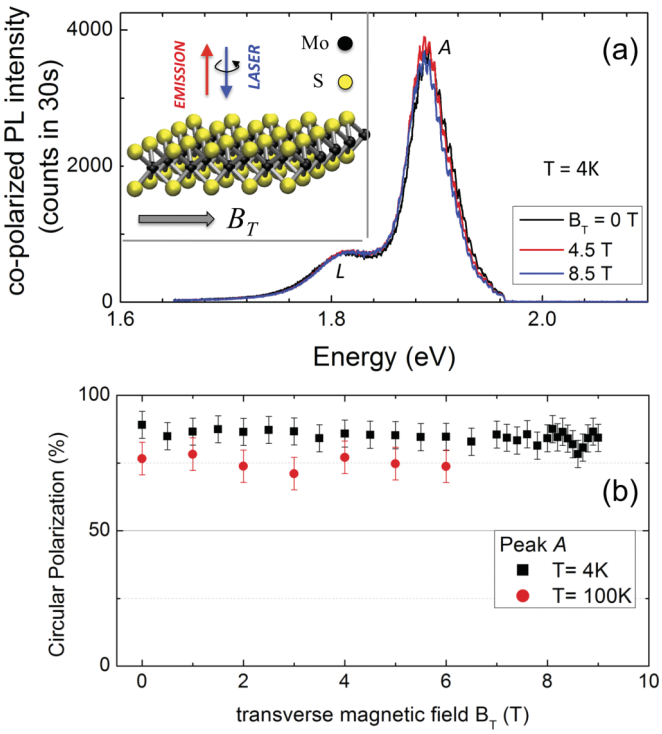

FIG. 3. (Color online) (a) Comparison of PL spectra of a single MoS_2 ML recorded for a transverse magnetic field $B_T = 0$, 4.5, and 8.5 T under otherwise identical experimental conditions using HeNe laser at 1.96 eV. Inset: Experimental geometry. (b) Measured PL circular polarization degree of the PL as a function of the applied transverse magnetic field B_T for $\boldsymbol{A}$ exciton at $T = 4$ K (squares) and at $T = 100$ K (circles).

because the radiative recombination rate is fast compared to the combined rates of the processes necessary to emit σ^- polarized light (i.e., change in k-valley, spin, and orbital angular momentum).[23]

A second crucial experimental test for the stability of the optically created valley polarization is the application of a transverse magnetic field. The spin quantization axis is chosen along the light propagation direction, i.e., perpendicular to the MoS_2 layer. as indicated in the inset of Fig. 3(a), where the magnetic field B_T is applied in the MoS_2 plane. In a classical picture for free carrier spins, the application of a magnetic field perpendicular to the spin quantization axis results in a precession of the spin around the applied field. As a result, the spin component along the quantization axis measured via the PL polarization degree in the circular basis would strongly decrease and eventually average out to zero in standard Hanle experiments.[14] With this simple picture in mind the constant polarization observed at $T = 4$ K in transverse magnetic fields up to 9 T and at $T = 100$ K in a field of $B_T = 6$ T shown in Fig. 3(b) seems very surprising. Again one needs to take into account the very unusual MoS_2 band structure, as discussed below.

Discussion. Both series of experiments detailed in Figs. 1 and 3 show robust PL polarization following σ^+ polarized laser excitation, i.e., the processes leading to a change in the valley state for both conduction and valence carriers and hence σ^- polarized emission are not very efficient. The emission is based on the dipole allowed recombination of a conduction electron with a valence hole, which we have detailed in Fig. 2(a). The main contribution to the strong optical absorption, which is reported to be nearly 10%,[3–5,11] comes from the Mo d orbitals (characterized by α), taking into account the contribution of transitions involving states in adjacent cells in k space. β characterizes the minute contribution of the p orbitals ($L = 1$) to the p-d hybridized VB states. The local trigonal symmetry of electron states in monolayer MoS_2 at $K_\pm$ points is C_{3h} in Koster notation,[24] and we have accordingly labeled the states using the corresponding group representations to which they belong. This leads us to predict the following: (i) The only symmetry allowed coupling introduced by a transverse magnetic field B_T is in principle between VB $\boldsymbol{A}$ and VB $\boldsymbol{B}$, and between VB $\boldsymbol{A}$ and CB, all of the same valley. This coupling would *not* change the emitted light polarization. In addition, the large energy difference between these bands makes this coupling vanishingly small. (ii) B_T does not couple states of inequivalent K_+ and K_- valleys. If the states indeed have the predicted symmetry, even a strong transverse field B_T would result in a constant emission polarization when increasing B_T. Our results seem to validate this prediction, even at elevated temperatures of 100 K in a field of $B_T = 6$ T as shown in Fig. 3(b), in addition to the initial reports in Ref. 12 for small fields.

Note that we do not have a clear spectral signature that would allow identifying the exciton charge state as suggested in Ref. 11. We therefore assume, in accordance with the intriguing polarization properties, the existence of neutral X^0 and/or negatively charged excitons X^-. The negatively charged exciton X^- consists of two electrons in a singlet state and an unpaired hole. Measuring the PL polarization allows monitoring directly the orientation of the hole spin as electron-hole Coulomb exchange effects essentially cancel out. For the X^0, following $\sigma^\pm$ photon absorption, bright excitons with a total (pseudo)spin of +1 or −1 are created. Dipole allowed optical transitions conserve the spin. So if only one of the carriers (electron or hole) flips, the X^0 becomes dark and nonradiative recombination might be favored. An electron spin flip is energetically feasible based on (nearly) degenerate conduction states. Hole spin flips, at the center of the investigation here, involve changing valley and are hence far less likely. To observe PL polarization change from the recombination of an exciton, both carriers have to be flipped (the exciton spin flips as a whole).[14] Importantly, to observe σ^- emission following optical excitation with σ^+ light involves for both X^0 and the X^- a hole spin flip by going from valley K_+ to K_-. In this context, changing the temperature has several consequences:

(i) Phonon assisted intervalley scattering ($K_+ \rightarrow K_-$) can be activated, since the average occupation number of acoustic and optical phonons increases for modes with wave vector $q \simeq |K_+ - K_-|$, thus increasing the probability of intervalley transfer for both electrons and holes.

(ii) As the temperature is increased, the band gap decreases,[6] but the laser energy in Fig. 1 is kept constant at 1.96 eV, which is very close to resonance with the top VB $\boldsymbol{A}$ to the bottom of the CB direct transition at $T < 50$ K. In a simple, independent particle picture, when raising the temperature, carriers increasingly further away from the K_+ point are optically injected[25] and the consistently high PL polarization observed in Fig. 1(a) indicates that the chiral valley selectivity is, as predicted, very high throughout the

valley.[9] At room temperature the laser is close to resonance with VB ***B*** with the opposite spin in the same valley. Note that this does not change the emission polarization (still σ^+) if the K_+ valley is populated, which could explain why we still measure 40% polarization at 300 K. To fully understand the origin of the remaining PL polarization, observed in different degrees in previous reports,[11,12] time resolved measurements should be employed in the future to extract the exact ratio of the radiative lifetime as compared to the valley/spin lifetime that determines the steady state PL polarization. Also, the fidelity of valley initialization at 300 K could be strongly improved in future experiments by using a laser energy closer to the ***A*** to CB resonance. We record a higher polarization at elevated temperatures than the MoS_2 ML on BN investigated in Ref. 11, indicating that the substrate material influences the optoelectronic properties of atomically flat MoS_2.

(iii) Due to the increase of the electron average kinetic energy, the average k-linear terms responsible for the electron spin splitting increase, while the elastic collision time decreases within a given valley. This may lead to an overall decrease of the conduction electron-spin relaxation time.[14] However, we reemphasize that an intervalley transfer both for electrons *and* holes is necessary to observe PL polarization decay.

The exact role of the strong Coulomb interaction also deserves further attention. Strong excitonic effects in this system close to the ideal two-dimensional confinement limit have been predicted[26,27] with exciton binding energies of $E^{2D}_{Ryd} \approx 800$ meV (Bohr radius $a_B \approx 1$ nm), which raises questions concerning the most reliable determination of the direct band gap of MoS_2.

Conclusion. The robust polarization observed at elevated temperatures and in transverse magnetic fields up to 9 T is a strong indication that optically created carriers remain during their radiative lifetime in the k-space valley selected via the excitation laser helicity, in agreement with the very recently predicted coupled spin and valley physics in monolayers of MoS_2.[8–10] Also, as changing spin state means changing valley in k space for valence states, the spin states are, as the valley index, very robust, which makes these results very interesting for future valley Hall coupled to spin Hall measurements and should encourage further research in this direction.[28]

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