Giant Paramagnetism-Induced Valley Polarization of Electrons in Charge-Tunable Monolayer $MoSe_2$

Patrick Back, Meinrad Sidler, Ovidiu Cotlet, Ajit Srivastava, Naotomo Takemura, Martin Kroner, and Atac Imamoğlu
Institute of Quantum Electronics, ETH Zürich, CH-8093 Zürich, Switzerland

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For applications exploiting the valley pseudospin degree of freedom in transition metal dichalcogenide monolayers, efficient preparation of electrons or holes in a single valley is essential. Here, we show that a magnetic field of 7 T leads to a near-complete valley polarization of electrons in a $MoSe_2$ monolayer with a density 1.6×10^{12} cm^{-2}; in the absence of exchange interactions favoring single-valley occupancy, a similar degree of valley polarization would have required a pseudospin g factor of 38. To investigate the magnetic response, we use polarization resolved photoluminescence as well as resonant reflection measurements. In the latter, we observe gate voltage dependent transfer of oscillator strength from the exciton to the attractive Fermi polaron: stark differences in the spectrum of the two light helicities provide a confirmation of valley polarization. Our findings suggest an interaction induced giant paramagnetic response of $MoSe_2$, which paves the way for valleytronics applications.

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Transition metal dichalcogenide (TMD) monolayers such as $MoSe_2$ represent a new class of two-dimensional (2D) direct band-gap semiconductors [1–4] exhibiting an ultralarge exciton binding energy E_{exc} in the order of 0.5 eV [5–9] and finite Berry curvature that leads to the valley Hall effect [10–12] as well as a modification of the exciton spectrum [13,14]. Investigation of one of the most interesting features of this material system, namely, the valley pseudospin degree of freedom [15], requires a high degree of valley polarization of electrons or holes. Previous experiments demonstrated a finite degree of electron valley polarization [16,17] that is consistent with the single-particle valley Zeeman effect [16,18,19]. While circularly polarized excitation ensures that the excitons are generated in a single valley [20–22], significant transfer of valley polarization from excitons to itinerant electrons or holes [23,24] has not been observed.

Here, we report a strong paramagnetic response of a two-dimensional electron system (2DES) in a charge-tunable monolayer $MoSe_2$ sandwiched between two hexagonal boron-nitride (h-BN) layers [Fig. 1(a)]. Figure 1(b) shows the corresponding single-particle energy-band diagram when an external magnetic field B_z is applied along the direction perpendicular to the plane of the monolayer, lifting the degeneracy of the electronic states in the $\pm K$ valleys. Remarkably, our experiments demonstrate that while the model depicted in Fig. 1(b) is qualitatively correct, the modest electron and exciton valley Zeeman splitting predicted by calculations [25] dramatically fails to explain the high degree of valley polarization we observe for a 2DES with an electron density $n_e = 1.6 \times 10^{12}$ cm^{-2} at $|B| = 7$ T. Concurrently, we find that the Zeeman splitting of elementary optical excitations out of a 2DES can be strongly modified by interaction and phase-space filling effects, yielding effective exciton-polaron g factors as high as 18.

To characterize the n_e dependence of the optical response at $B_z = 7$ T, we carried out polarization resolved photoluminescence (PL) experiments. Figures 2(a) and 2(b) show the PL spectrum of the $MoSe_2$ monolayer as a function of the gate voltage V_g for σ^+ and σ^- polarized emission upon excitation with a linearly polarized excitation laser at wavelength $\lambda_L = 719$ nm. For $V_g \geq V_{\mathrm{on},-K} = 100$ V the monolayer is devoid of free electrons ($n_e \simeq 0$). In this regime PL, which we attribute to radiative recombination of excitons bound to localized electrons (i.e., localized trions), exhibits a sizable degree of circular polarization where the ratio of the maximum peak intensities of σ^+ and σ^- polarized emission is $R_{\mathrm{PL}} \simeq 11$ [Fig. 2(c)]. We attribute the observed PL polarization, which vanishes completely at $B_z = 0$, to fast relaxation into the lowest energy optically excited states. As free electrons are injected into the sample ($V_g < V_{\mathrm{on},-K}$), we observe a dramatic increase (decrease) in σ^+ (σ^-) polarized PL [Fig. 2(d)]. The maximum value of R_{PL} in this regime exceeds 700; the suppression of PL at $\lambda = 760$ nm is so strong that in this V_g range the exciton emission at $\lambda = 748$ nm is the dominant source of σ^- polarized photons. Further increase of n_e ($V_g < V_{\mathrm{on},K} = 70$ V) results in a strong redshift of emission as well as a recovery of R_{PL} to the value observed in the absence of free electrons [Fig. 2(e)].

To explain V_g dependence of polarization resolved PL we recall that in $MoSe_2$ monolayers at low n_e, σ^+ (σ^-) trions are formed only when a $-K$ (K) valley electron binds to a K ($-K$) valley exciton [27]. A strong increase (decrease) in the observed σ^+ (σ^-) trion emission therefore indicates that the electrons in the range $V_{\mathrm{on},K} < V_g < V_{\mathrm{on},-K}$, corresponding to $0 < n_e < 1.6 \times 10^{12}$ cm^{-2}, exhibit a high degree of valley polarization. The fact that σ^- exciton PL is not reduced as V_g is

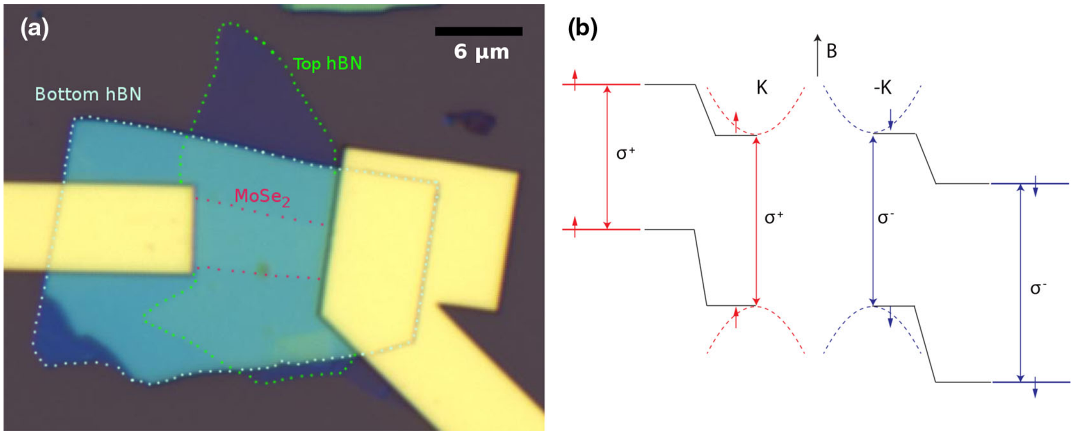

FIG. 1. A gate controlled $MoSe_2/h$-BN heterostructure under external magnetic field. (a), The sample consists of a 9 μm by 4 μm $MoSe_2$ monolayer sandwiched between two h-BN layers. Gate voltage applied between the gold contacts to the $MoSe_2$ layer and the highly doped Si substrate allows for controlling the electron density in the monolayer. (b) The single particle picture of conduction and valence band shifts under a magnetic field B_z applied perpendicular to the plane of $MoSe_2$. Assuming a large spin-orbit splitting, only the lowest (highest) energy conduction (valence) band is depicted. For $B_z > 0$, the exciton resonance in the K valley redshifts along with the conduction band minimum in the $-K$ valley. This opposite sign of the effective g factor of the excitons and electrons plays a key role in determining the absorption spectrum of $MoSe_2$ monolayers.

tuned below $V_{\text{on},-K}$ corroborates this conclusion. We remark that, due to spin-valley locking in $MoSe_2$, a valley polarized $n_e = 1.6 \times 10^{12}$ cm^{-2} corresponds to a Fermi energy of $E_F = 15$ meV (see Sec. V of the Supplemental Material [26]).

To verify the conclusions we draw from PL experiments, we measure white light reflection as a function of V_g. The reflection spectrum can be understood in the framework of Fermi polarons, which describe the many-body phenomena resulting from the attractive interaction between a quantum impurity (in our case a rigid exciton) and a fermionic bath. At vanishing n_e, the reflection spectrum is dominated by the exciton peak. As recent experiments [28] demonstrated, a new redshifted resonance emerges as n_e is increased: this attractive-polaron resonance [28,29] can be understood as a bound state of a trion and a Fermi-sea hole. Concurrently, the trion bound state acts as a Feshbach resonance that ensures repulsive interaction between free excitons and electrons. As a consequence, the exciton resonance blueshifts with increasing n_e: this is the repulsive polaron [28] resonance. A key prediction of the polaron model is the oscillator strength transfer from the repulsive to the attractive polaron as n_e increases.

In $MoSe_2$, spin-orbit interaction ensures spin-valley locking and that the bright exciton formation is due to excitation of an electron to the lowest energy conduction band. As stated earlier, the only bound trion state in $MoSe_2$ for low n_e and for vanishing B_z is the intervalley trion, which in turn implies that σ^+ (σ^-) excitons that occupy K ($-K$) valley states interact attractively only with electrons in the $-K$ (K) valley. Equivalently, if the electrons are valley polarized in the $-K$ (K) valley, only the σ^+ (σ^-) polarized absorption or reflection spectrum will show attractive and repulsive polaron resonances. Concurrently, the electron population in the $-K$ (K) valley will lead to a blueshift of the σ^- (σ^+) bare exciton resonance due to phase-space filling stemming from Pauli blocking.

Figure 3(a) [Fig. 3(b)] shows the normalized reflection spectrum of σ^+ (σ^-) polarized white light at $B_z = 7$ T that verifies the aforementioned predictions. More specifically, we observe that the σ^+ and σ^- polarized reflection spectra exhibit two striking differences in the range $V_{\text{on},K} < V_g < V_{\text{on},-K}$. First, the reflection spectrum of σ^+ shows an attractive polaron resonance whereas that of σ^- does not indicating that electrons predominantly occupy $-K$ valley states. Second, while the σ^+ attractive polaron exhibits a redshift with increasing n_e, σ^- exciton resonance shows a blueshift even though a corresponding σ^- attractive polaron resonance is absent. As we already indicated, strong electron pseudospin polarization in the $-K$ valley, would ensure that the $-K$ valley (σ^-) exciton resonance exhibits a blueshift due to Pauli blocking. The redshift of the attractive polaron is in turn fully consistent with the absence of a 2DES and the associated phase-space filling in the K valley. Overall, reflection spectra in this V_g range indicate (almost) complete valley polarization of electrons.

We model our structure as a parallel plate capacitor to determine the change in electron density as V_g is decreased from $V_{\text{on},-K}$ to $V_{\text{on},K}$:

$$\Delta n_e = (V_{\text{on},-K} - V_{\text{on},K})\varepsilon_0\epsilon/(eL) = 1.6 \times 10^{12}\ \text{cm}^{-2},$$

where ε_0, e, and $L/\epsilon = 101$ nm denote the vacuum permittivity, the electron charge, and the effective combined thickness of the insulating SiO_2 and h-BN layers separating the $MoSe_2$ flake from the back gate. The SiO_2 thickness is $\approx$285 nm with $\epsilon \approx 3.9$, for h-BN the thickness is $\approx$85 nm and $\epsilon_{h\text{-BN}} \approx 3$. Since for $V_{\text{on},-K} > V_g > V_{\text{on},K}$, electrons only occupy states in the $-K$ valley, Δn_e gives the maximum fully

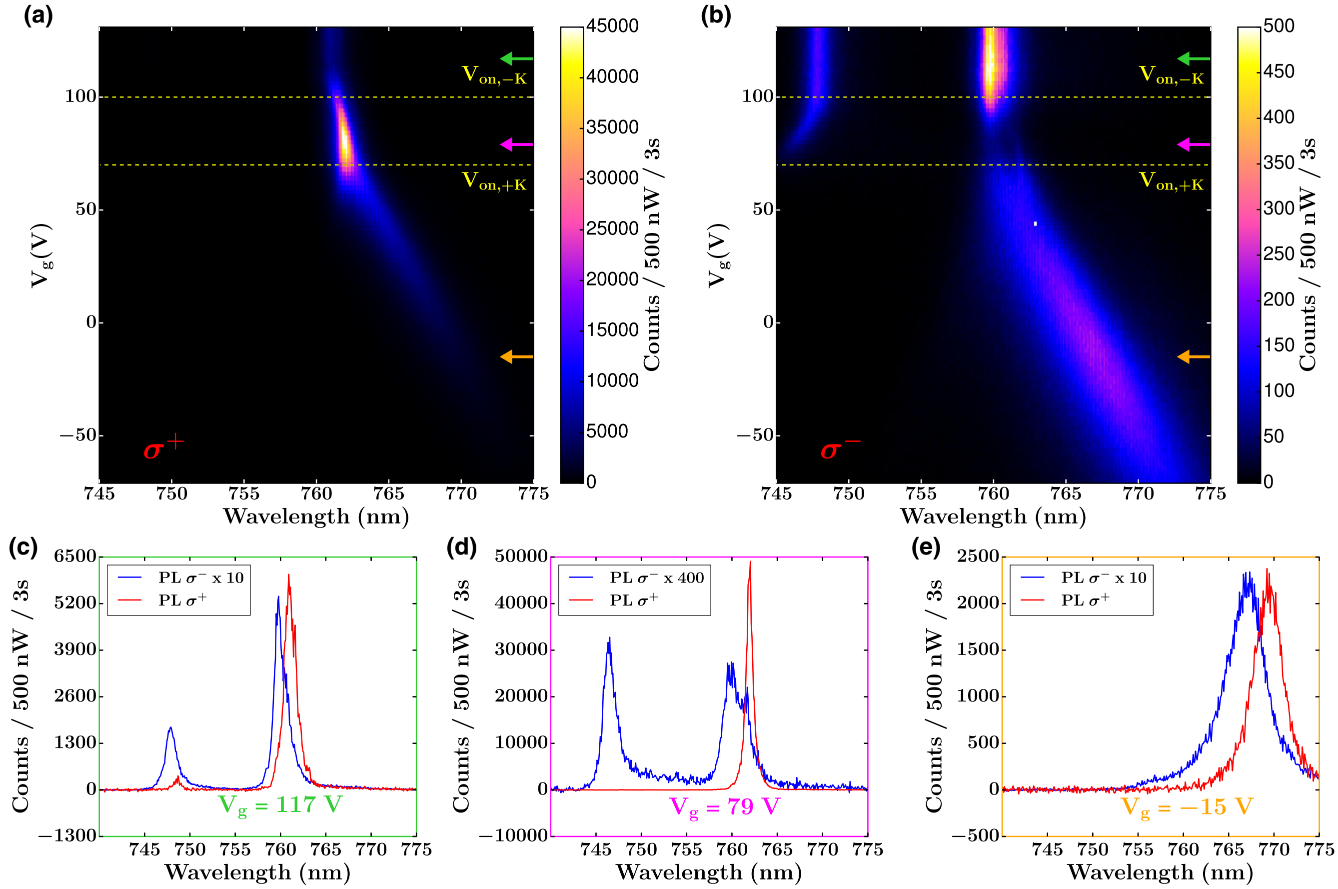

FIG. 2. Gate voltage dependent photoluminescence spectrum under a magnetic field of $B_z = 7$ T. (a) Gate voltage (V_g) dependent right-hand circularly polarized (σ^+) photoluminescence (PL) spectrum of a $MoSe_2/h$-BN heterostructure at $B_z = 7$ T under excitation by a linearly polarized 719 nm laser. The depicted V_g axis is shifted by 10 V to compensate for the hysteretic behavior we observe in the gate scans (see Supplemental Material [26]). (b) The corresponding PL spectrum for left-hand circularly polarized (σ^-). (c) The line cut through the σ^+ and σ^- PL spectra at $V_g = 117$ V $> V_{on,-K}$ show that the PL exhibits a sizable degree of polarization where the ratio of σ^+ and σ^- polarized PL intensities is $\simeq 11$. (d) The line cut through the σ^+ and σ^- PL spectra at $V_g = 79$ V shows that the degree of PL polarization increases dramatically to yield a ratio of σ^+ and σ^- polarized PL intensities $\simeq 700$. (e) The line cut through the σ^+ and σ^- PL spectra at $V_g = -15$ V where both valleys have high n_e. The ratio of the right- (σ^+) and left- (σ^-) hand circularly polarized PL intensities is reduced back to $\simeq 11$.

valley-polarized electron density. We estimate an uncertainty of $\pm 0.5 \times 10^{12}$ cm^{-2} for Δn_e, stemming from the accuracy of thickness measurement of the h-BN layer, as well as an uncertainty of ± 5 V in determination of $V_{on,\pm K}$ (see Sec. V of the Supplemental Material [26]).

We remark that reported theoretical predictions of single-particle electron valley g factors vary from -0.86 [30] to 5.12 [25]; if we were to take the latter value, we would obtain $\Delta n_e = 0.2 \times 10^{12}$ cm^{-2} at $B_z = 7$ T. The corresponding value that our experiments yield is a factor of 8 larger. In the absence of exchange interactions favoring single-valley occupancy, a similar degree of valley polarization would have required a pseudospin g factor of 38. The relatively abrupt loss of valley polarization at $V_g = 70$ V could be associated with the fact that E_F of the valley polarized electrons with density $n_e = 1.6 \times 10^{12}$ cm^{-2} exceeds the conduction band spin-orbit splitting. We also note that the B_z dependence of valley polarized n_e shows saturation for $|B_z| \geq 5$ T (see Fig. S3 of the Supplemental Material [26]), indicating a deviation from a purely paramagnetic response that is consistent with super-paramagnetism [31]. We speculate that reduced screening and relatively heavy electron mass may ensure that exchange and correlation energies in monolayer $MoSe_2$ exceed kinetic energy even for densities of order 1.6×10^{12} cm^{-2}, resulting in the observed giant paramagnetic response at $T = 4$ K. Higher quality samples at lower temperatures could be used to investigate if an interaction induced phase transition to a ferromagnetic state is possible [32].

The spectra depicted in Figs. 3(a) and 3(b) reveal that the valley Zeeman splitting of the excitonic transitions can be drastically modified when $n_e > 0$. Figure 3(c) shows overlayed line cuts through the normalized reflection spectra for $V_g = 127$ V $> V_{on,-K}$ ($n_e \simeq 0$). The blueshift of the σ^- exciton line with respect to the σ^+ exciton stems from the valley Zeeman effect and the extracted exciton g factor $g_{exc} = 4.4$ is in excellent agreement with previous reports [16,18,19,33].

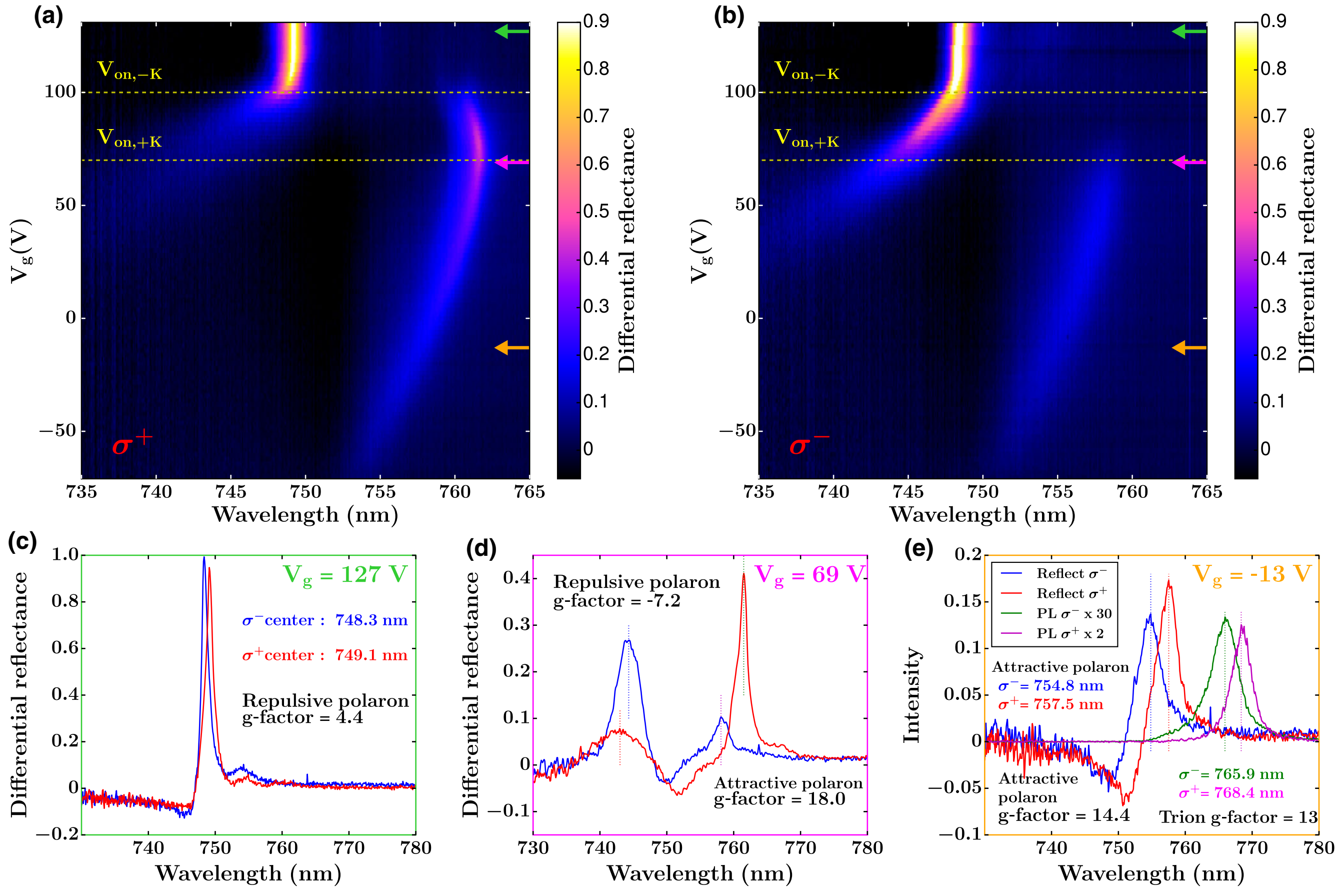

FIG. 3. Polarization resolved reflection spectrum under a magnetic field of $B_z = 7$ T. (a) Gate voltage (V_g) dependent right-hand circularly polarized (σ^+) white light reflection spectrum of the $MoSe_2$/h-BN heterostructure at a magnetic field of $B_z = 7$ T. For $V_g \leq V_{\text{on},-K} = 100$ V (yellow dashed horizontal line), we observe a blueshift of the exciton resonance whereas the strength of the attractive polaron resonance increases as it redshifts. (b) Reflection spectrum as in (a) but now for left-hand circularly polarized (σ^-) light. Only for $V_g \leq V_{\text{on},K} = 70$ V, oscillator strength transfer to the attractive polaron is observed. Whereas the exciton oscillator strengths of the σ^+ and σ^- transitions for $V_g > V_{\text{on},-K}$ are nearly identical, the σ^+ attractive polaron is much stronger than its σ^- counterpart for $V_{\text{on},K} < V_g < V_{\text{on},-K}$. (c) The differential reflection spectrum of both σ^+ and σ^- light at $V_g = 127$ V: the two resonances have nearly identical shape and strength but their energies differ by 1.8 meV, yielding a g factor of 4.4. (d) The differential reflection spectrum as in (c) but now at $V_g = 69$ V: the splitting between the attractive polaron resonances is 7.3 meV, which corresponds to a g factor of $\simeq$18. The σ^+ exciton or repulsive polaron energy on the other hand is lower than that of σ^- by $\simeq$2.9 meV, yielding a g factor of -7.2. These results demonstrate that exciton-electron interactions strongly modify the magneto-optical response of $MoSe_2$ monolayers. (e) The differential reflection as well as PL spectrum of both σ^+ and σ^- light at $V_g = -13$ V.

Figure 3(d) shows the reflection spectra for $V_g = 69$ V ($n_e = 1.7 \times 10^{12}$ cm^{-2}). The σ^+ reflection spectrum for this V_g is dominated by the attractive polaron with a smaller weight on the repulsive polaron or exciton branch, whereas the opposite is true for the σ^- spectrum. An estimation of the peak splittings for the attractive and repulsive polaron resonances in Fig. 3(d) yield effective corresponding g factors of $g_{\text{att-pol}} = 18$ and $g_{\text{rep-pol}} = -7.2$. This drastic change in the effective g factors of elementary optical excitations as compared to the $n_e = 0$ case depicted in Fig. 3(c) is a direct consequence of the aforementioned interaction and phase-space filling effects: in the limit $n_e(-K) \gg n_e(K)$, the red (blue) shift of the attractive (repulsive) polaron energy $\Delta_\pm^{\text{att}} \propto n_e(\mp K)$ [$\Delta_\pm^{\text{rep}} \propto n_e(\mp K)$] stemming from exciton-electron interactions [28] is larger for σ^+ excitation. On the other hand, the blueshift due to phase-space filling [also $\propto n_e(\mp K)$] is more significant for σ^- resonances. For the attractive polaron the two contributions add, leading to a large splitting. For the repulsive polaron on the other hand, the interaction and phase-space filling contributions compete, resulting in an eventual sign change of $g_{\text{rep-pol}}$. These observations provide a further confirmation of the Fermi-polaron model of excitonic excitations [28]. As we show in the Fig. S4 of the Supplemental Material [26], the measured polaron energy splittings vary almost linearly with B_z.

Figure 3(e) shows the σ^+ and σ^- PL together with the differential reflection spectrum at $V_g = -13$ V where both valleys have $n_e > 3 \times 10^{12}$ cm^{-2}. In addition to the sizable resonance energy differences, we find that the g factors observed in reflection and PL are not identical

($g_{\text{att-pol}} = 14.4$ and $g_{\text{trion}} = 13.0$). These differences provide yet another proof that the elementary excitations determining absorption or reflection measurements are different from those that are relevant for PL. We remark that an increase in trion Zeeman splitting for such high n_e as compared to the vanishing free electron density limit has been previously observed and described as being a consequence of partial electron valley polarization [16].

Our experiments establish that using $B_z = 7$ T, it is possible to valley polarize electron densities exceeding 1.6×10^{12} cm^{-2} in a TMD monolayer. This remarkable observation points to a giant magnetic susceptibility, presumably stemming from exchange interactions, enabling new possibilities for the control and manipulation of the valley degree of freedom. The enhancement of the total detected PL intensity by a factor of $\simeq 8$ for $n_e \sim 1.0 \times 10^{12}$ cm^{-2} suggests a possible way to increase the radiative quantum efficiency of $MoSe_2$. We speculate that this PL enhancement is a consequence of the bright trion having lower energy than the dark intervalley exciton.

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