Giant paramagnetism induced valley polarization of electrons in charge-tunable monolayer MoSe$_2$

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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 Tesla leads to a near-complete valley polarization of electrons in MoSe$_2$ monolayer with a density $1.6 \times 10^{12}$ 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 exceeding 40. 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.

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 ultra-large exciton binding energy $E_{\text{exc}}$ in the order of 0.5 eV [5-9] and finite Berry curvature that leads to valley Hall effect [10,11] as well as a modification of the exciton spectrum [12,13]. Investigation of one of the most interesting features of this material system, namely the valley pseudospin degree of freedom [14,15], has been hampered by the difficulty in obtaining a high-degree of valley polarization of free electrons or holes [16]. While circularly polarized excitation ensures that the excitons are generated in a single valley [17,19], significant transfer of valley polarization from excitons to itinerant electrons or holes 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 (hBN) layers (Fig. 1A). Figure 1B 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. 1B is qualitatively correct, the modest electron and exciton valley Zeeman splitting predicted by calculations neglecting interaction effects fails dramatically to explain the high-degree of valley polarization we observe for a 2DES with an electron density $n_e = 1.6 \times 10^{12} \text{ cm}^{-2}$ at $|B| = 7 \text{ T}$. 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 $B_z = 7 \text{ Tesla}$, we first carried out polarization resolved photoluminescence (PL) experiments. Figure 2A and 2B show the PL spectrum of the MoSe$_2$ monolayer as a function of the gate voltage $V_g$ for $\sigma^+$ and $\sigma^-$ polarized emission upon excitation with a linearly polarized excitation laser at wavelength $\lambda_L = 719 \text{ nm}$. For $V_g \geq V_{on,-K} = 100 \text{ V}$ 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 sizeable degree of circular polarization where the ratio of the maximum peak intensities of $\sigma^+$ and $\sigma^-$ polarized emission is $R_{PL} \simeq 11$ (Fig. 2C). 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 ($V_g < V_{on,-K}$), we observe a dramatic increase (decrease) in $\sigma^+$ ($\sigma^-$) polarized PL (Fig. 2D). The maximum value of $R_{PL}$ in this regime exceeds 700; the suppression of trion PL at $\lambda = 760 \text{ nm}$ is so strong that in this $V_g$ range the exciton emission at $\lambda = 748 \text{ nm}$ is the dominant source of $\sigma^-$ polarized photons. Further increase of $n_e$ ($V_g < V_{on,K} = 70 \text{ V}$) results in a strong red-shift of emission as well as a recovery of $R_{PL}$ to the value observed in the absence of free electrons (Fig 2E).

The highly nontrivial $V_g$ dependence of polarization resolved trion PL can be understood by recalling that in MoSe$_2$ monolayers at low $n_e$, $\sigma^+$ ($\sigma^-$) trions are formed only when a $-K$ ($K$) valley electron binds to a $K$ ($-K$) valley exciton. A strong increase (decrease) in the observed $\sigma^+$ ($\sigma^-$) trion emission therefore indicates that the electrons in the range $V_{on,K} < V_g < V_{on,-K}$, corresponding to free electron density range $0 < n_e < 1.6 \times 10^{12} \text{ cm}^{-2}$, exhibit a high degree of valley polarization. The fact that $\sigma^-$ exciton PL is not reduced as $V_g$ is tuned below $V_{on,-K}$ corroborates this conclusion.

To verify the conclusions we draw from PL experiments, we measure white light reflection as a function of $V_g$. Figure 3A (3B) shows the normalized reflection spectrum of $\sigma^+$ ($\sigma^-$) polarized white
light at $B_z = 7$ Tesla: in agreement with recent experiments [21], the spectrum exhibits a dominant exciton line at vanishing mobile electron densities $n_e \sim 0$. As free electrons are introduced into the monolayer, a red-shifted attractive polaron resonance becomes prominent. Increasing the $n_e$ further results in a sharp blue-shift and broadening of the exciton line, which has been identified as the repulsive polaron [21, 22]. The interaction between excitons and electrons that lead to polaron formation can be described as being associated with a trion channel [21]. As a consequence, $\sigma^+$ ($\sigma^-$) attractive polaron resonance is observed if and only if the $-K$ ($K$) valley has a finite electron density, which in turn, as stated earlier, ensures that $\sigma^+$ ($\sigma^-$) trions could be formed.

The $\sigma^+$ and $\sigma^-$ polarized reflection spectra exhibit two striking differences in the range $V_{on,K} < V_g < V_{on,-K}$. First, the reflection spectrum of $\sigma^+$ shows an attractive polaron resonance whereas that of $\sigma^-$ does not – indicating that electrons predominantly occupy $-K$ valley states. Second, while the $\sigma^+$ attractive polaron exhibits a red-shift with increasing $n_e$, $\sigma^-$ exciton resonance shows a blue-shift even though a corresponding $\sigma^-$ attractive polaron resonance is absent. If there is strong electron pseudospin polarization in $-K$ valley, we would expect the $-K$ valley ($\sigma^-$) exciton resonance to exhibit a blue-shift due to phase-space filling stemming from the Pauli blocking of the electronic states that would otherwise contribute to exciton formation. The red-shift 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. We therefore conclude that the reflection spectra in this $V_g$ range is fully consistent with near-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 $V_{on,-K}$ to $V_{on,K}$:

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

where $\varepsilon_0$, $e$ and $L/\varepsilon = 101$ nm denote the vacuum permittivity, the electron charge and the effective combined thickness of the insulating SiO$_2$ and hBN layers separating the MoSe$_2$ flake from the back gate. Since for $V_{on,-K} > V_g > V_{on,K}$, electrons only occupy states in $-K$ valley, $\Delta n_e$ gives the maximum fully valley polarized electron density. We estimate an uncertainty of $0.5 \times 10^{12} \text{cm}^{-2}$ for the absolute value of $\Delta n_e$; this uncertainty stems from the accuracy of our measurement of the thickness of the hBN layer, as well as our inability to determine $V_{on,\pm K}$ precisely.

We remark that reported theoretical predictions of single-particle electron valley g-factors vary from $-0.86$ [23] to 5.12 [20]; if we were to take the latter value, we would obtain $\Delta n_e = 0.2 \times 10^{12} \text{ cm}^{-2}$ at $B_z = 7$ T. The corresponding value that our experiments yield is a factor of 8 larger, demonstrating that a simple paramagnetic response based on single-particle parameters
cannot describe the inferred degree of valley polarization. We also note that the $B_z$-dependence of valley polarized $n_e$ shows saturation for $|B_z| \geq 5$ T, indicating a deviation from a purely paramagnetic response that is consistent with super-paramagnetism \cite{24}. 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 $1.6 \times 10^{12}$ cm$^{-2}$, resulting in the observed giant paramagnetic response at $T = 4$ K. Investigation of higher quality samples at lower temperatures could be used to investigate if an interaction induced phase transition to a ferromagnetic state is possible \cite{25}.

The reflection spectra depicted in Fig. 3A,B reveal that the valley Zeeman splitting of the excitonic transitions can be drastically modified when $n_e > 0$. Figure 3C shows overlaid line-cuts through the normalized reflection spectra for $V_g = 127$ V $> V_{on,-K}$ ($n_e \simeq 0$). The blue-shift of the $\sigma^-$ exciton line with respect to the $\sigma^+$ exciton stems from the valley Zeeman effect and the extracted exciton g-factor $g_{exc} = 4.4$ is in excellent agreement with previous reports \cite{26-29}.

Figure 3D shows the reflection spectra for $V_g = 69$ V ($n_e = 1.7 \times 10^{12}$ cm$^{-2}$). The $\sigma^+$ reflection spectrum for this $V_g$ is dominated by the attractive polaron with a smaller weight on the repulsive polaron/exciton branch, whereas the opposite is true for $\sigma^-$ spectrum. An estimation of the peak-splittings for the attractive and repulsive polaron resonances in Fig. 3D yield effective corresponding g-factors of $g_{att-pol} = 18$ and $g_{rep-pol} = -7.2$. This drastic change in the effective g-factors of elementary optical excitations as compared to the $n_e = 0$ case depicted in Fig. 3C is a direct consequence of 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 $\Delta_{\pm}^{att} \propto n_e(\mp K)$ ($\Delta_{\pm}^{rep} \propto n_e(\pm K)$) stemming from exciton-electron interactions \cite{21} is larger for $\sigma^+$ excitation. On the other hand, the blue-shift due to phase-space filling (also $\propto n_e(\mp K)$) is more significant for $\sigma^-$ 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 $g_{rep-pol}$. These observations provide a further confirmation of the Fermi-polaron model of excitonic excitations \cite{21}.

Figure 3E shows the $\sigma^+$ and $\sigma^-$ 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 sizeable resonance energy differences, we observe that the attractive polaron and trion g-factors are not identical ($g_{att-pol} = 14.4$ and $g_{trion} = 13.0$). These differences provide yet another proof that the elementary excitations determining absorption/reflection measurements are different from those that are relevant for PL.
Our experiments establish that using moderate $B_z$, it is possible to valley polarize electron densities exceeding $1.6 \times 10^{12}$ 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. Interesting open questions include the temperature dependence of the magnetic response and its possible relation to the theoretical prediction of spontaneous valley polarization in silicon inversion layers [25]. In parallel, our measurements unequivocally demonstrate the validity of the polaron picture for describing resonant absorption/reflection experiments. Finally, the enhancement of the total detected PL intensity by a factor of $\approx 8$ for $n_e \sim 1.0 \times 10^{12}$ cm$^{-2}$ suggests a possible way to increase the radiative quantum efficiency of MoSe$_2$.

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FIG. 1: A gate controlled MoSe$_2$/hBN heterostructure under external magnetic field. (A), The sample consists of a 9$\mu$m by 4$\mu$m MoSe$_2$ monolayer sandwiched between two hBN layers. The heterostructure is placed on top of a 285 nm thick SiO$_2$ layer, which in turn is on top of highly doped Si substrate. A gate voltage applied between the gold contacts to the MoSe$_2$ layer and the highly doped Si 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. The contributions from spin, intra-cellular and inter-cellular currents ensure that for $B_z > 0$, the exciton resonance in the K valley red-shifts 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.
FIG. 2: Gate voltage dependent photoluminescence spectrum under moderate magnetic fields. (A), Gate voltage ($V_g$) dependent right-hand circularly polarized ($\sigma^+$) photoluminescence (PL) spectrum of a MoSe$_2$/hBN heterostructure at $B_z = 7$ Tesla 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. (B), The corresponding PL spectrum for left-hand circularly polarized ($\sigma^-$). (C), The line cut through the $\sigma^+$ and $\sigma^-$ PL spectra at $V_g = 117$ V > $V_{on,\sigma^+}$ show that the PL exhibits sizeable degree of polarization where the ratio of $\sigma^+$ and $\sigma^-$ polarized PL intensities is $\approx 11$. (D), The line cut through the $\sigma^+$ and $\sigma^-$ PL spectra at $V_g = 79$ V shows that the degree of PL polarization increases dramatically to yield a ratio of $\sigma^+$ and $\sigma^-$ polarized PL intensities $\approx 700$. (E), The line cut through the $\sigma^+$ and $\sigma^-$ PL spectra at $V_g = -15$ V where both valleys have high $n_e$. The ratio of the right ($\sigma^+$) and left ($\sigma^-$) hand circularly polarized PL intensities is reduced back to $\approx 11$. 
FIG. 3: Polarization resolved reflection spectrum under moderate magnetic fields. (A), Gate voltage ($V_g$) dependent right-hand circularly polarized ($\sigma^+$) white light reflection spectrum of the MoSe$_2$/hBN heterostructure at a magnetic field of $B_z = 7$ Tesla. For $V_g \leq V_{on,-K} = 100$ V (yellow dashed horizontal line), we observe a blue-shift of the exciton resonance whereas the strength of the attractive polaron resonance increases as it red-shifts. (B), Gate voltage dependent reflection spectrum as in (a) but now for left-hand circularly polarized ($\sigma^-$) light. For $V_g \leq V_{on,-K}$, the exciton line starts to blue-shift. Only for $V_g \leq V_{on,K} = 70$ V, oscillator strength transfer to the attractive polaron is observed. Whereas the exciton oscillator strength of the $\sigma^+$ and $\sigma^-$ transitions for $V_g > V_{on,-K}$ are nearly identical, the $\sigma^+$ attractive polaron is much stronger than its $\sigma^-$ counterpart for $V_{on,K} < V_g < V_{on,-K}$. (C), The differential reflection spectrum of both $\sigma^+$ and $\sigma^-$ 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 $\sigma^+$ exciton/respulsive polaron energy on the other hand is lower than that of $\sigma^-$ 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 $\sigma^+$ and $\sigma^-$ light at $V_g = -13$ V: both the energy and the g-factor of the resonances observed in reflection/absorption and PL are different.