Spin-defect characteristics of single sulfur vacancies in monolayer MoS₂

A. Hötger¹, T. Amit², J. Klein³, K. Barthelmí³, T. Pelini³, A. Delhomme⁴, S. Rey⁵, M. Potemski⁶,⁷, C. Faugeras¹, G. Cohen¹, D. Hernangómez-Pérez¹, T. Taniguchi⁸, K. Watanabe⁸, C. Kastl¹, J. J. Finley¹, S. Refaely-Abramson⁹, A. W. Holleitner¹ and A. V. Stier¹,¹⁰

Single spin-defects in 2D transition-metal dichalcogenides are natural spin-photon interfaces for quantum applications. Here we report high-field magneto-photoluminescence spectroscopy from three emission lines (Q₁, Q₂, and Q*) of He-ion induced sulfur vacancies in monolayer MoS₂. Analysis of the asymmetric PL lineshapes in combination with the diamagnetic shift of Q₁ and Q₂ yields a consistent picture of localized emitters with a wave function extent of ~3.5 nm. The distinct valley-Zeeman splitting in out-of-plane B-fields and the broadening of dark states through in-plane B-fields necessitates spin-valley selectivity of the defect states and lifted spin-degeneracy at zero field. Comparing our results to ab initio calculations identifies the nature of Q₁ and Q₂ and suggests that Q* is the emission from a chemically functionalized defect. Analysis of the optical degree of circular polarization reveals that the Fermi level is a parameter that enables the tunability of the emitter. These results show that defects in 2D semiconductors may be utilized for quantum technologies.

INTRODUCTION

Spin-defects in host crystals can be fundamental building blocks for quantum technologies, such as computing, sensing or communication.¹⁻⁴ For instance, color centers in diamond have been investigated since the early 1980s, of which the nitrogen vacancy (NV) center is the most prominent example.⁵,⁶ In this defect, the crystal field splitting lifts the ground state spin degeneracy and provides the required unique quantum degree of freedom to form an addressable two-level system.⁷⁻¹⁰ In addition, NV centers are single photon sources¹¹ and therefore constitute excellent building blocks for future quantum photonic circuits. However, a key prerequisite for such applications is the ability to position defects deterministically. This is a challenge for defects in 3D crystals, such as single NV centers, as they can be positioned either vertically or laterally with high precision, but not both simultaneously.¹⁴⁻¹⁷ This disadvantage can be overcome by creating optically addressable spin-defects in 2D host crystals. Localized single photon emission in 2D materials was first discovered in monolayer WSe₂, a prototypical member of the semiconducting 2D transition metal dichalcogenides (TMDs).¹⁸⁻²² Subsequently, single photon emitters were discovered in hexagonal boron nitride (hBN).²³ Contrasted with hBN, TMDs have strong light-matter coupling²⁴ and locked spin-valley physics²⁵ which provides a natural spin-photon interface. Moreover, the 2D semiconducting host crystal has enabled new possibilities to engineer and manipulate these defects²⁶⁻²⁸, which led to further advances in quantum devices, such as quantum light emitting diodes²⁹⁻³¹.

First approaches for the deterministic creation of quantum emitters in 2D materials made use of strain potentials, for instance induced by a textured substrate.³²⁻³⁸ This results in a local bandstructure modulation in the host crystal, limited by the bending radius of the material, yet the latter approach intrinsically lacks reproducibility. Furthermore, the confining potential often breaks crystal symmetries, leading to the loss of valley optical selection rules. A higher degree of spatial resolution and reproducibility can be achieved by using the accuracy of electron-beam or focused ion beam irradiation.³⁹⁻⁴³ Specifically, He-ions can be precisely focused and create optically active point defects in monolayer MoS₂ with a precision better than 10 nm.⁴⁴ In photoluminescence (PL) spectroscopy, spectrally narrow emission lines appear about 200 meV red-shifted from the neutral exciton of He-ion irradiated MoS₂.⁴⁵ Second order correlation measurements unambiguously showed single photon emission from single He-ion irradiation sites, which in turn could be related to the generated point defects.⁴⁶⁻⁴⁸ A specific advantage is that these defects can be implanted into more complex, electronic device heterostructures, allowing for the electrical control of quantum emission.²⁸ The microscopic origin of various localized emission centers is currently a matter of debate. One specific defect complex, which is predominant in He-ion irradiated MoS₂, is the chalcogen vacancy, where one sulfur atom has been removed from the host lattice.³⁴ Sub-gap quantum emission from this defect was suggested to originate from a relaxation cascade where an optical interband excitation creates a bound electron-hole pair that subsequently localizes into the defect and radiatively recombines.⁴⁸ However, pristine defect states have been predicted to be essentially spin degenerate.⁴⁷,⁴⁹ Moreover, other relaxation pathways, such as defect-to-band transitions are in principle possible, and, due to the...
strong spin-orbit interaction in the host MoS₂, considerations with respect to spin-valley physics have yet to be taken into account. In this manuscript, we investigate three distinct emission lines of He-ion induced sulfur vacancies created in monolayer MoS₂ by high-field magneto-optical spectroscopy, which has previously been shown to be an important tool to investigate the excitonic spin-valley physics in 2D TMDs. We identify the bands involved in the optical quantum emission and show that an energy-dependent degree of hybridization between atom-like defect states and the MoS₂ bandstructure leads to varying degree of valley selectivity for the distinct electron-hole transitions. Our results display that sulfur vacancies in monolayer MoS₂ are spin-defects that can be tailored to specific quantum applications.

RESULTS

Photoluminescence from sulfur vacancies in monolayer MoS₂

The left hand side of Fig. 1a shows the schematic of the sample under investigation. A monolayer MoS₂ is encapsulated in hBN, fabricated by standard dry viscoelastic stamping methods (see Methods for details). Subsequently, a focused He-ion beam is scanned across the sample, creating predominantly sulfur vacancies in the MoS₂. Our sample is He-ion irradiated with a pitch of ~2 μm, which allows us to selectively investigate individual irradiated locations (see Supplementary Fig. 1a). Typical defect PL spectra at 1.7 K and zero magnetic field are shown in Fig. 1b. The dominant feature at 1.75 eV, labeled Q1, has previously been identified as a single photon emitter associated with an unpassivated sulfur vacancy. In this manuscript, we discuss only those locations which contained a single Q1 line, generally the case for the sample under investigation. The low energy tail of Q1 is attributed to the coupling of a localized state to acoustic phonons in MoS₂. Analysis of the lineshape with an independent boson model allowed the determination of the effective Bohr radius of this localized state to be ≈2–3 nm. A weak secondary feature about 30 meV red-shifted from the zero phonon line (ZPL) of Q1, can be assigned to a phonon replica due to a local phonon mode (LPM) of this defect center. Emission line Q2 forms in a distinct energy band ≈75 meV red-shifted from Q1, while another emission line Q* appears ≈50 meV blue-shifted. Both lines generally appear fainter as compared to Q1, while the lineshape of all features are similar. The statistical evaluation of all emission lines investigated throughout the sample clearly indicates these three inhomogeneously broadened, yet distinct, emission bands (see Supplementary Fig. 1c). Our zero B-field spectroscopy therefore establishes the observed emission lines to originate from localized defect centers. This is consistent with predictions of six spinor wave functions due to an atomistic defect associated with a sulfur vacancy resulting from its C₃ᵥ symmetry, where two spin-split bands are above the Fermi energy and one is below it (see Supplementary Fig. 10). As sketched in Fig. 1c and discussed in detail below, we unambiguously identify Q1 as an excitonic transition predominantly between defect induced states (cD1/cD2 ↔ vD) at the Γ point, with significant hybridization across the Brillouin zone and specifically at the K/K' points. This spread

Fig. 1  Defect luminescence of He-ion irradiated monolayer MoS₂. a Sketch of the monolayer MoS₂ encapsulated in hexagonal boron nitride (hBN) illustrating the He-ion irradiation and the out-of-plane magneto-spectroscopy scheme. b Typical low-temperature photoluminescence (PL) spectra of the quantum emission Q1, Q2, and the local phonon mode (LPM) of Q1. c Illustration of the MoS₂ bandstructure at the K and Γ valleys including the defect states of a sulfur vacancy. The modified bandstructure shows flat defect-related levels vD, cD2, and cD1. The red (blue) color represents the spin-up (spin-down) eigenstate of the associated band. A small spin splitting of the defect states is observed in our calculations at the K/K’ valleys, as discussed in the main text. At B₀ = 0 T, the Fermi energy E_F lies below the unoccupied defect states. Solid circles mark significant defect states. d Degree of circular polarization (DCP) versus B for Q1 and Q2. The blue shaded area highlights the ±10% experimental uncertainty. The oscillations in the DCP below ~15 T are predominantly due to fringe field induced Faraday rotation in the low temperature objective. The solid lines are fits to the data with Eq. (1) for Q1 and a Boltzmann statistics fit for Q2 (see Supplementary Fig. 5).
in momentum-space originates from the localized character of the sulfur vacancy, as shown by the calculated wave function distributions associated with the electronic defect levels cD1, cD2 and vD (see Supplementary Fig. 10). The wave functions are primarily composed of transition metal d-orbitals and therefore contain the spin-valley physics of monolayer MoS2 throughout the Brillouin zone.

For the energetically lower lying emission Q2, we identify the superposition of transitions between both spin-up/down defect induced conduction band states (cD1) and the MoS2 valence band (VB) at the K/K'-points in the Brillouin zone. Although Q2 is also excitonic, the transitions are con along the valleys of the host MoS2. At each positive magnetic field, we probe the circular dichroism by detecting the PL for σ and σ+'polarization, which we calibrate with the well known valley Zeeman splitting of the neutral exciton in MoS2 (see Supplementary Fig. 2).

As such, we minimize the impact of positional sample drift with respect to the beam path in very high magnetic fields. From the faint appearance of the negatively charged trion in the PL spectra and the value of the valley Zeeman splitting for the neutral exciton (μ_b = -2.8 ± 0.1 μ_b), we conclude that our MoS2 crystal is weakly electron doped n = 5 × 10¹¹ cm⁻². Figure 2a depicts typical polarization resolved PL spectra of Q1 and the LPM at B⊥ = 0 T. Unlike strain induced quantum emitters in monolayer TMDs, the He-ion-induced defects show no valley dichroism at zero magnetic field (Fig. 1d). This is expected for the C₃ᵥ symmetry of an unperturbed sulfur vacancy with defect-to-defect transitions at the Γ-point. The left (right) panel of Fig. 2b shows the normalized PL of Q1 versus B⊥ for σ(σ') polarized detection. The position of the ZPL exhibits a monotonic blue-shift with increasing magnetic field for both polarizations. We plot the PL peak position in Fig. 2c and find that the average peak position for

Out-of-plane magnetic field measurements on defects in MoS₂

In order to investigate the nature of the observed emission bands, we employ magneto-PL spectroscopy, where the magnetic field B⊥ up to 27 T is applied perpendicular to the 2D sample plane and parallel to the optical beam path (Faraday geometry). The sample was mounted in a He-exchange gas cryostat with a bath temperature of T_bath = 4.2 K. The sample was excited with a linearly polarized continuous wave (CW) laser at a wavelength of 515 nm and power of ~10 μW, focused to a beam spot of ~1 μm. The linear polarization excites interband transitions in both K/K' valleys of the host MoS2. At each positive magnetic field, we probe the valley Zeeman splitting of the neutral exciton. As an example, the DCP of Q1 reveals essentially no resolved magneto-spectroscopy. Thus, we probe via circular polarization (DCP) tending towards unity at the highest fields. Q2 polarizes already at low fields. The observation that these emission lines show valley dichroism at finite magnetic field necessitates the lifting of the spin degeneracy, and we further proof in detail below that the spin degeneracy of the defect states in the K/K' valleys is already lifted at zero magnetic field. Thus, the sulfur vacancy in MoS2 can be considered as a spin-defect.

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![Fig. 2 Out-of-plane magnetic field B⊥ dependent photoluminescence of defect luminescence Q1](image-url)  

**a** Low-temperature photoluminescence (PL) spectra of defect luminescence Q1 at zero out-of-plane magnetic field (B⊥) for σ(σ') polarized detection. The spectra were normalized to their maximum intensity.  

**b** PL versus B⊥ for Q1. The left (right) panel shows the σ(σ') polarization. The spectra were normalized to their maximum intensity.  

**c** The fitted position of the ZPL of Q1 shows a diamagnetic shift of 1.0 ± 0.1 meV T⁻².  

**d** Valley Zeeman splitting of Q1 versus B⊥. The black dashed line shows a fit to the data with a Zeeman splitting of μ_b = 0.1 ± 0.1 μ_b.  

**e** Bandstructure of MoS2 with a periodic sulfur-vacancy extracted from DFT calculations. The color code denotes the total magnetic moment at each k-point.  

**f** Density of states (DOS) plot of the Brillouin zone, showing energetically narrow densities at the defect levels.  

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Out-of-plane magnetic field measurements on defects in MoS₂

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$\sigma^+$ and $\sigma^-$ detection $\frac{1}{2} (E_{\sigma^+} + E_{\sigma^-})$ can be fitted with a quadratic function ($-B^2$) with a prefactor of $\sigma = 1.0 \pm 0.1 \text{ meV } T^{-2}$. The quadratic-in-$B$ blueshift is consistent with the expected magnetic shift of a bound particle in 2D, $\Delta E_{\text{mag}} = e^2 (r^2) B^2 / 8m_0a^2$. The root mean square radius in the plane of the 2D material is expressed as $r_{rms} = \sqrt{8m_0a/e}$, where $m_0$ is the reduced mass of the particle and $e$ the elementary charge, respectively. The observed magnetic shift coefficient of Q1 is roughly 5 x larger than that of the neutral MoS$_2$ exciton. Assuming the reduced mass for the neutral exciton and Q1 are the same, $(m_0 = 0.275m_0)$, the observed magnetic shift yields a particle size $r_{rms} = 3.5 \text{ nm}$, consistent with the findings of the independent boson model discussed above. The valley Zeeman splitting, defined from the difference $E_{\sigma^+} - E_{\sigma^-} = \mu B$ is shown in Fig. 2d. In contrast to other quantum emitters in 2D materials, the Q1 emission shows little, but experimentally detectable, positive valley Zeeman splitting of $\mu_{\perp Q1} = +0.1 \pm 0.1 \text{ meV}$. Such a vanishing Zeeman splitting has recently been observed on a quantum emission and was attributed to a quasiparticle transition between pristine conduction band and in-gap defect state. However, the latter study does not provide a full evaluation on the excitonic effects, which are crucial for magneto-spectroscopy in TMDs. In order to get a first insight into the nature of the Q1 emission line, Fig. 2e shows the DFT bandstructure of MoS$_2$ with a 2% sulfur vacancy density. The pristine bandstructure of MoS$_2$ is essentially unaffected by the presence of the sulfur vacancies. However, additional electronic states lie within the bandgap (CD1, CD2), as well as in the valence band (VD) of MoS$_2$. These states are relatively flat in k-space, which yields a high joint density of states for defect-to-defect transitions in this system (Fig. 2f), particularly at the $\Gamma$-point. For a pure defect-to-defect transition at the $\Gamma$-point, we expect exactly zero valley Zeeman splitting due to the vanishing of the valley selectivity. In turn, the finite valley Zeeman splitting is consistent with a Q1 emission dominated by defect-to-band transitions at the K/K'-points, which we discuss in detail below.

Although we find $\mu_{\perp Q1} = 0$, we measure a large degree of circular polarization (Fig. 1d) at high magnetic fields, calculated from the integrated PL intensities of both helicities $(I_{\sigma^+} - I_{\sigma^-})/(I_{\sigma^+} + I_{\sigma^-})$. This $B$-field induced circular polarization requires spin polarized states to participate in the optical transition. The measured DCP at $B = 0$ T is within the experimental uncertainty of $\pm 10\%$ (indicated by the shaded area in Fig. 1d). The uncertainty originates from spectral jitter as well as uncompensated Faraday rotation of the linearly polarized excitation light combined with imperfectly aligned $\lambda/4$ and linear polarizers in the detection path. In our understanding, the intensities of the $\sigma^+$ and $\sigma^-$ polarized transition in either the $K$ or the $K'$-valley are weighted with the probability of the defect level at $E_{\text{Q2}}$ to be occupied by an electron of the Fermi sea using the Fermi-Dirac $f_{\text{FD}}$ distribution. In turn, we assume following expression to fit the DCP as a function of the applied magnetic field.

$$D\text{CP}(B) = \frac{f_{\text{FD}}(E_{\sigma^+} - E_{\text{Q2}}) - f_{\text{FD}}(E_{\sigma^-} - E_{\text{Q2}})}{f_{\text{FD}}(E_{\sigma^+} + E_{\text{Q2}}) + f_{\text{FD}}(E_{\sigma^-} + E_{\text{Q2}})},$$

(1)

with the Zeeman shift of the CD2 states in the K/K' valleys to be $\mu_{\text{CD2}} = B$ and $E_{\text{CD2,0}}$ the energy of state CD2 at zero field. Fitting the data of Q1 in Fig. 1d with Eq. (1) (see line in Fig. 1d) yields $\mu_{\text{CD2}} = 2.6 \pm 0.5 \text{ meV}$, with the error given by the systematic error of our polarization alignment in the high-magnetic field setup. Moreover, the fit assigns CD2 to be above the Fermi energy $E_F$ at $B = 0$ T, with $E_{\text{CD2}} - E_F = 3.2 \pm 0.7 \text{ meV}$. We note that the ab initio calculations as in Fig. 2e determine $E_{\text{Q2}}$ to be 0.86$\mu_B$, which is again clearly positive. For the experimental (ab initio) value, the Zeeman shift of CD2 at 22.5 T equals $-3.4 \text{ meV}$ ($1.12 \text{ meV}$), which is larger than the thermal energy of $\sim 0.7 \text{ meV}$ at 4.2 K. In our understanding, this explains that the DCP can be detected at high magnetic fields at the given temperature. We note that this interpretation is corroborated by a gate-tunable device where the DCP changes sign by reversing the polarity of $B$ (see Supplementary Fig. 4). As a consequence, an applied magnetic field lifts the spin degeneracy of Q1. Moreover, a characteristic blue-shift of the quantum emission with increasing charge carrier density suggests the defects to be charge neutral (see Supplementary Fig. 4). Based on these findings, Fig. 2g summarizes the interpreted bandstructure at $K/K'$ and $\Gamma$ for zero and finite $B$. With increasing magnetic fields, the spin-up state of CD2 in the K valley (lowest defect state in the bandgap at the $K$-point) is pushed away from the Fermi edge, which decreases the possibility for it to be occupied with an electron from the Fermi edge. This increases the part of $\sigma^+$ polarized light emitted at the $K$-point and eventually polarizes the overall emission. Conversely, at the $K'$-point, the spin-down defect state is the lowest defect state in the bandgap and is pushed towards the Fermi edge. Therefore, the intensity of $\sigma^-$ polarized light subsequently diminishes. From the combined experimental observations of small valley Zeeman splitting and strongly $B_z$-dependent DCP, we identify Q1 as an excitonic emission of a neutral sulfur vacancy in MoS$_2$ between hybridized defect-to-defect and defect-to-band transitions and relate the observed DCP to a combination of magnetic field induced Zeeman shifts and occupation effects.

The $B_z$-dependence of the LPM emission mirrors that of Q1, as expected, with a diamagnetic shift of $\sigma = 1.00 \pm 0.04 \text{ meV } T^{-2}$, a negligible $\mu_{\lambda}$ and the same DCP trend as Q1 (see Supplementary Fig. 3). The similar magnetic field dependence of Q1 and LPM firmly supports the claim that the LPM emission is a replica of the same optical transition as Q1 with the additional emission of a phonon related to a local mode of the defect center.

We now turn to the magneto-spectroscopy of the emission line Q2. Figure 3a shows polarization resolved spectra of the quantum emission line Q2. Panel a shows the PL of Q2 versus $B_z$ for $\sigma^+$ (left panel) and $\sigma^-$ polarized detection (right panel). b The Zeeman splitting of Q2 shows a Zeeman splitting of $\mu = +1.3 \pm 0.1 \mu_B$. c Position of the ZPL of Q2 versus the applied magnetic field ($\mu_B$), showing a diamagnetic shift of $\sigma = 1.1 \pm 0.2 \text{ meV } T^{-2}$.  

**Figure 3** Out-of-plane magnetic field $B_z$ dependent photoluminescence of defect luminescence Q2. a PL of Q2 versus $B_z$ for $\sigma^+$ (left panel) and $\sigma^-$ polarized detection (right panel). b The Zeeman splitting of Q2 shows a Zeeman splitting of $\mu = +1.3 \pm 0.1 \mu_B$. c Position of the ZPL of Q2 versus the applied magnetic field ($\mu_B$), showing a diamagnetic shift of $\sigma = 1.1 \pm 0.2 \text{ meV } T^{-2}$.
In-plane magnetic luminescence of defect luminescence Q1 and Q2. a Sketch of the in-plane magnetic field \( B_1 \) configuration (Voigt Geometry). No polarization optics were used in the detection path. b Emission of Q1 remains bright for all fields. c The in-plane field reveals a second state Q2\( _d \) energetically below Q2. The white dashed lines are guides to the eye for the expected in-plane Zeeman shift of Q1 and the dark-bright-splitting of Q2. The dark-bright splitting \( \Delta_{DB} \approx 1.4 \text{ meV} \) for Q2 is calculated with Eq. (2). d The quadratic dependence of the emission ratio between Q2\( _d \) and Q2 indicates the brightening of a dark ground state. e Sketch of the defect levels with the possible optical transitions for Q1 and Q2 at finite \( B_1 \).

\[
\Delta B_j = \left( \Delta \mu_B \pm \Delta \mu_B' \right) \left( 1 \pm (\mu_j \cdot B_j)^2 \right),
\]

where \( \Delta \mu_B \) is the dark-bright splitting at \( B_j = 0 \) T and \( \mu_j \) is the magnitude of the in-plane magnetic moment. The white dashed line in Fig. 4c depicts Eq. (2) with \( \Delta \mu_B = 1.4 \text{ meV} \) and \( \mu_j = 1 \mu_B \). The excellent agreement between data and the calculated difference of the bright and dark transition of Q2, which is simply given by the Zeeman splitting of the cD1 band (\( \Delta \mu_{cD1} = 2.2 \mu_B \)), extracted from Fig. 4. Finally, the combined magneto-spectroscopy in the Faraday and Voigt geometry unambiguously identifies Q2 as a spin conserving transition from the cD1 state to the respective MoS\( _2 \) valence band in the K/\( K' \) valley.

The fact that the emission line Q1 is energetically higher than Q2, while the diamagnetic shift, and therefore the binding energy of Q1 and Q2 are essentially the same, requires the defect band vD to be located below the valence band edge of MoS\( _2 \), as sketched in Fig. 4e.47-49.

First-principles calculations on monolayer MoS\( _2 \) with embedded sulfur vacancies

To deepen the insight into the nature of Q1 and Q2, we theoretically investigate exciton transitions in monolayer MoS\( _2 \) with embedded sulfur vacancies using ab initio calculations. Details about the calculation can be found in the Supplementary Note 4 as well as the Methods section of refs. 47,48,64. In brief, we use many-body perturbation theory within the GW-Bethe Salpeter approximation with explicit spin-orbit coupling and spinor wave functions and compute the many-body Zeeman splitting following ref. 65. Figure 5a shows the mean calculated Zeeman splitting for an excitonic absorption as a function of excitation energy. Line colors represent the calculated absorption strength for...
As well as the hole bands (νD and VB) are illustrated in energetic order under the consideration of the lifted spin degeneracy at the contributing to excitons in the energy range associated with Q2, namely in the magenta shaded area in function of excitation energy. The colorcode on the line represents the absorption strength at each energy.

The electron bands (cD1 and cD2), as well as the hole bands (νD and VB) are illustrated in energetic order under the consideration of the lifted spin degeneracy at the νD = K, Γ, and νD = K’-points. The electron-hole transitions contributing to excitons in the energy range associated with Q1, namely in the gray shaded area in a. The transitions are shown for three selective k-points, K (b, e), Γ (c, f), and K’ (d, g).

At the Γ and K’-points, only band-to-defect transitions are contributing, whereas at the K-point, defect-to-defect transitions are dominating. Specifically, we find contributions from the lower valence band to defect band cD2 at the K’-points in absorption. Unlike Q1, the calculations suggest that the Q2 emission is only comprised of band-to-defect transitions at the K’-points. The hybridization of Q1 with the energetically lower Q2 emission can be deduced from the band-to-defect contributions at the K’-points.

**DISCUSSION**

In order to characterize the defect luminescence, Q1 and Q2 of He-ion irradiated monolayer MoS2 towards spin-defect properties, we combine our experimental observations with theoretical insight. He-ions create sulfur vacancies, which induce flat defect bands throughout the pristine bandstructure of monolayer MoS2. As a result, a high joint DOS for defect-to-defect transitions is created. At the K/K’-points however, the defect νD lies below the valence band maximum of MoS2, such that defect-to-band transitions are more likely. In high-field magneto-spectroscopy, we observe a diamagnetic shift of the defect luminescence Q1 and Q2, which is consistent with a bound particle of ~3.5 nm. This localized character will result in optical transitions covering a significant momentum-space. Thus, the GW-Bethe-Salpeter equation is useful for gaining deeper understanding into the defect-induced transitions. Here we find that the nature of Q1 and Q2 can
be viewed as mixed states of defect-to-defect and defect-to-band transitions. The level of this admixture determines the magnetic moment and valley selectivity of these hybridized transitions.\textsuperscript{47,64} We find a dominant contribution of band-to-band transitions at the $K'/K$-points for the energy interval of Q2, whereas Q1 additionally acquires sizeable defect-to-defect character from the $\Gamma$-point. These contributions at the $\Gamma$-point induce a breaking of the valley selectivity, reflected in the small valley Zeeman splitting of this transition. For both Q1 and Q2, however, we find a magnetic-field dependent DCP, which necessitates spin conserving optical transitions. The distinct behavior of the DCP is explained by the defect-to-band transitions at the $K'/K$-points contributing to Q1 and Q2. The in-plane magneto-spectroscopy reveals a spin-forbidden dark ground state for Q2, which unambiguously proofs the lifted spin degeneracy of the defect bands at the $K'/K$-points even at zero magnetic field. In contrast, the absence of a dark state for Q1 can be explained by the significant portion of transitions happening at the $\Gamma$-point, where the defect bands are spin degenerate due to Kramers' theorem.

In conclusion, the combination of in-plane and out-of-plane magneto-spectroscopy identifies the Q1 emission as a defect-to-defect transition with admixture of Q2, which is dominated by transitions from in-gap defect states to the pristine valence band of MoS$_2$. This outcome suggests tailored modification of the defect luminescence through either charging or chemical modification (Q$^+$, see Supplementary Note 2 and 3). We show that the defect states at $K'/K$ are split at zero magnetic field, a property that characterizes the sulfur vacancy in MoS$_2$ as a spin defect with desirable features for possible quantum technological applications.

METHODS

Sample preparation

MoS$_2$ bulk crystals were purchased from HQGraphene, and the hBN crystals were provided by Takashi Taniguchi and Kenji Watanabe from NIMS, Japan. Monolayers of MoS$_2$ and few-layer hBN were obtained by mechanical cleavage of bulk crystals. The thin crystals were stacked with the viscoelastic transfer method onto a Si substrate with 285 nm of thermal SiO$_2$. After the assembly of the desired heterostructure, namely the MoS$_2$ encapsulated in hBN, the helium ion microscope (HIM) Orion NanoFab from Zeiss was used to precisely irradiate the sample with He-ions at 30 kV in an array pattern with a pitch of 2 $\mu$m. The dose was chosen to get a high yield of single sharp emitter lines for Q1. For the photoluminescence measurements in Fig. 1b an excitation wavelength of 639 nm and a power of 550 nW at a bath temperature of 1.7 K was used. The photoluminescence signal was guided on a nitrogen cooled CCD via a 300 grooves/mm dispersive grating. A long pass filter was used to extinguish the directly reflected excitation laser emission.

Magneto-spectroscopy

The magneto-photoluminescence measurements were performed in a cryostat cooled to 4.2 K surrounded by a resistive magnet. For excitation, a laser diode with an emission wavelength of 515 nm and a power of 550 nW at a bath temperature of 1.7 K was used. The photoluminescence signal was directed rephasing the GW results to a k-grid of 3 × 3 × 1 k-grid and an energy cutoff of 25 Ry for the dielectric matrix. Electron-hole coupling and exciton energies were calculated using BerkeleyGW by solving the Bethe-Salpeter equation (BSE)\textsuperscript{70,71} by interpolating the GW results to a k-grid of 6 × 6 × 1 with a dielectric matrix which was calculated with a 5 Ry cutoff and summation over 1798 bands. Quasi-particle magnetization corrections and many-body excitonic Zeeman splitting were evaluated from the GW-BSE results following recently derived methods.\textsuperscript{65,72} More details are presented in the Supplementary Note 4.

DATA AVAILABILITY

Data included in this manuscript will be made available upon reasonable request to the authors.

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AUTHOR CONTRIBUTIONS
A.H., J.K., J.J.F., A.W.H., and A.S. conceived and designed the experiments. T.A, G.C., D.H., and S.R-A. performed the DFT-GW and BSE calculations. S.R. and J.K. prepared the sample. K.W. and T.T. provided high-quality hBN bulk crystals. A.H., A.S., T.P., A.D., C.F., J.K., and K.B. performed the optical measurements. A.H. analyzed the data. C.K., M.P., and C.F. contributed interpreting the data. A.H. and A.S. wrote the manuscript with input from all coauthors.

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Correspondence and requests for materials should be addressed to A. V. Stier.

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