Letter

Magneto photoluminescence measurements of tungsten disulphide monolayers

Jan Kuhnert, Arash Rahimi-Iman and Wolfram Heimbrodt

Faculty of Physics and Materials Sciences Center, Philipps-University 35032 Marburg, Germany

E-mail: wolfram.heimbrodt@physik.uni-marburg.de

Received 24 November 2016, revised 19 December 2016
Accepted for publication 23 December 2016
Published 12 January 2017

Abstract

Layered transition-metal dichalcogenides have attracted great interest in the last few years. Thinned down to the monolayer limit they change from an indirect band structure to a direct band gap in the visible region. Due to the monolayer thickness the inversion symmetry of the crystal is broken and spin and valley are coupled to each other. The degeneracy between the two equivalent valleys, K and K’, respectively, can be lifted by applying an external magnetic field. Here, we present photoluminescence measurements of CVD-grown tungsten disulphide (WS$_2$) monolayers at temperatures of 2 K. By applying magnetic fields up to 7 T in Faraday geometry, a splitting of the photoluminescence peaks can be observed. The magnetic field dependence of the A-exciton, the trion and three bound exciton states is discussed and the corresponding g-factors are determined.

Keywords: g-factor, WS$_2$, 2D materials

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last few years, a new class of monolayer materials has emerged after the successful rise of graphene: transition metal dichalcogenides (TMDCs). The most popular representatives are MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. They have attracted great interest from physicists all over the world due to their outstanding physical properties [1–6]. Thinned down to single layers, they change from an indirect band gap semiconductor in the bulk to a direct band gap semiconductor in the monolayer regime with its direct band gap located in the K and K’ valley of the Brillouin zone [7, 8]. The optical properties of these materials have already been widely studied. One very interesting aspect, to name but a few, is that in the monolayer limit the spin and valley degrees of freedom are coupled. This allows to selectively address the K or the K’ valley by the helicity of the incident light [9–12]. To break the degeneracy of the energetically equivalent K and K’ valleys, an external magnetic field can be applied that couples to the magnetic moments perpendicular to the hexagonal lattice structure of each valley. Due to the different sign of the magnetic moments in the K and K’ valley, the two components split into two Zeeman components which spectrally can be distinguished. Up to now investigations on the magnetic properties of transition metal dichalcogenides have been reported [9, 10, 13–17].

So far, the excitonic g-factors for monolayers have been determined for neutral excitons (A-exciton) to be ($-3.94 \pm 0.04$) in WS$_2$ [18], ($-4.0 \pm 0.2$) in MoS$_2$ [18], ($-3.7 \pm 0.2$), ($-3.7 \pm 0.15$), ($-4.0 \pm 0.5$), ($-1.57$ up to $-2.86$) in WSe$_2$ [13–15, 19], and ($-3.8 \pm 0.2$) [10, 19] and ($-4.1 \pm 0.2$) [9] in MoSe$_2$, respectively. Reported values for the g-factor of the second excitonic transition (B-exciton) are only available for bulk material: ($-3.99 \pm 0.04$) for WS$_2$ and ($-4.65 \pm 0.17$) for MoS$_2$ [18]. For charged excitons (trions) in WSe$_2$ effective g-factors of ($-4.0 \pm 0.5$) and ($-6.28 \pm 0.32$) [14, 15] are reported, and for MoSe$_2$ g-factors of ($-3.8 \pm 0.2$) [10] and ($-4.1 \pm 0.2$) up to ($-6.2 \pm 0.2$) depending on the doping level [9] are reported, respectively. To our knowledge there have been no reports on trionic g-factors for transition metal disulphides yet.
It is worth to note that the photoluminescence (PL) of the TMDCs, however, often consists of various bands: Besides the A-exciton and trion, the bi-exciton and even bound exciton states can be observed, which can show a similar but yet not identical behaviour in external fields. In this work we perform polarization-resolved PL measurements of WS$_2$ monolayers in magnetic fields up to 7 T, in order to determine the $g$-factors of these various excitonic species in this host lattice.

2. Materials & methods

2.1. Sample

The WS$_2$ monolayer samples were grown via CVD at 875 °C on a silicon substrate covered by SiO$_2$. The substrate size was approximately $20 \times 10 \text{ mm}^2$ and the precursors are WO$_3$ powder and H$_2$S using purified Argon as carrier gas. The WS$_2$ monolayers are triangularly shaped and have a size of roughly $30 \times 30 \mu\text{m}^2$.

2.2. Raman measurements

To find the monolayer flakes on the sample Raman measurements were performed prior to measuring the magneto PL. The Raman measurements were carried out at room temperature using a standard Olympus BX41 microscope equipped with a Raman setup. A 80 mW small band 514.5 nm argon-ion laser was focused on the sample via a 100 x standard objective. The holographic notch filter allows to measure Raman shifts bigger than 200 cm$^{-1}$ relative to the laser wavenumber which is sufficient to measure the characteristic $A_{1g}$ and $E_{2g}$ Raman lines at $\sim 420 \text{ cm}^{-1}$ and $\sim 350 \text{ cm}^{-1}$, respectively.

2.3. Magneto luminescence measurements

For the magneto-PL (M-PL) measurements, the sample was glued into an Oxford cryostate that is equipped with a superconducting liquid helium cooled magnet delivering fields up to 7 Tesla. The fields can either be applied in Voigt or in Faraday geometry. For our measurements, we solely used the Faraday geometry, for which the applied magnetic field is parallel to the k-vector of the emitted light field and therefore perpendicular to the sample surface. The sample was excited by a 150 mW 532 nm diode-pumped intracavity-frequency-doubled Nd:YAG laser, which was focussed onto the sample via a lens to a spot size of approximately $25 \times 25 \mu\text{m}^2$. PL was collected, collimated and focussed via lenses onto the 10 $\mu\text{m}$ entrance slit of a 1250 mm spectrometer equipped with a 1200-lines grating and detected by a highly sensitive thermoelectrically-cooled silicon CCD. The achieved resolution was about 0.4 meV. In order to distinguish between $\sigma^+$- and $\sigma^-$-polarized light, a linear-polarizer plate was placed in front of the entrance slit of the spectrometer and a rotateable quarter-wave plate in front of the polarizer to select the desired circular polarization. All measurements were carried out at a sample temperature of 2 K.

Figure 1. Raman measurement of the WS$_2$ sample with the characteristic $A_{1g}$ and $E_{2g}$ Raman lines. The smaller energy difference for the monolayer mode (63.46 cm$^{-1}$) can be clearly seen compared to the bulk mode (68 cm$^{-1}$). The experiments were carried out at room temperature.

Figure 2. Photoluminescence measurements of the WS$_2$ monolayer with applied magnetic fields up to 7 Tesla in Faraday geometry using a 532 nm laser for excitation. The PL is detected in a $\sigma^+$- and $\sigma^-$-polarized basis. The sample temperature was kept at 2 K. The spectra are normalized and shifted vertically for clarity.

3. Results & discussion

Raman spectroscopy is an excellent tool to identify the number of layers in few-layer TMDC flakes. Figure 1 displays typical Raman spectra of such samples. Here, the Raman signal of bulk WS$_2$ is compared with the one from our CVD sample, both recorded at room temperature. The $A_{1g}$ line, which is the out of plane mode, is located at 416.70 cm$^{-1}$ and the $E_{2g}$
line, the inplane mode, is located at 353.24 cm$^{-1}$ in case of the CVD sample, respectively. The difference between both modes (indicated by dashed vertical lines in the diagram) is 63.46 cm$^{-1}$ which is a good indicator for a monolayer regime. The respective separation in the case of the bulk sample is 68 cm$^{-1}$. The spectra are normalized to the $E_{21}^{1}$ line for the sake of clarity. The observed change in the relative separation ratio has been reported [20] and has been attributed to dielectric screening [21].

The M-PL measurements at a temperature of 2 K are shown in figure 2 for left-circularly ($\sigma^-$, red solid lines) and right-circularly polarized ($\sigma^+$, blue solid lines) luminescence following laser excitation at 2.33 eV. The pump density amounted to 15 kW cm$^{-2}$. The spectra are normalized and offset by a constant value to form a waterfall diagram. The increasing splitting of the PL peaks with increasing magnetic field strength is clearly visible, here.

It is also apparent that with increasing fields the $\sigma^-$-component grows relative to the $\sigma^+$-component, becoming more pronounced on the higher-energy side of its peak.

It is obvious that the obtained spectrum is governed by an overlap of various bands. To get a deeper insight in the individual PL bands, the intensity of our representative spectrum is plotted both in linear (left) and logarithmic scale (right) in figure 3. We denote the individual peaks as generally accepted. The highest-energetic peak at 2.102 eV is assigned to the exciton in agreement with earlier papers [22, 23], where the exciton was found at 2.09 eV at a temperature of 5 K. The trion emission peak is centered at 2.06 eV. The visibility of the exciton and trion peaks at elevated energies indicates a high quality of the CVD sample, as this peak is absent in some earlier studies [24, 25]. We should mention, however, that the intravalley/intervalley triplet splitting [26] could not be resolved so far in CVD grown samples since the photoluminescence linewidth used to be about 20 meV. The most intense PL contribution (centered at 2.025 eV) stems from a superposition of three bands which we ascribe to bound exciton transitions (labeled BE1, BE2 and BE3).

By applying a magnetic field in Faraday geometry, the $\sigma^-$-component shifts towards higher energies, while the $\sigma^+$-component is shifted to lower energies. Exemplarily, we show the spectra for the highest applied field of 7 T in $\sigma^-$ (top) and $\sigma^+$ (bottom) circular polarization in figure 4. To determine the effective $g$-factors of all the peaks, the spectra have been fitted by means of multiple gaussian shaped curves. One curve is used for each peak component, i.e. exciton, trion, defect-bound exciton 1,2,3, respectively. It should be mentioned, that the exciton and trion could also be fitted using a Lorentzian curve yielding the same peak position and energy splitting. Using Gaussian-shaped bands yield a better overall matching of the experimental data similar as found by Plechinger et al [27]. We ascribe this to inhomogeneous broadening caused by lateral band structure fluctuations caused by the various deep centers. Firstly, the PL spectrum in the case of zero external magnetic field was fitted to determine both the energetic positions and the full width at half maximum (FWHM) values. The exciton and trion peaks exhibit a substantially smaller FWHM (16.95 meV and 18.84 meV, respectively) than the defect-bound exciton-emissions (23.19 meV, 22.37 meV, and 21.38 meV). The FWHMs were kept unchanged for the fitting procedure in higher fields to reduce the number of free parameters. The best fitting results for both 7T $\sigma^-$ (top) and 7T $\sigma^+$ (bottom) are exemplarily shown in figure 4. By fitting the $\sigma^-$ and $\sigma^+$ spectra for all applied fields ranging up to 7 T the peak position and amplitude for each excitonic species could be determined. It should be mentioned that the diamagnetic shift of the transitions does not need to be taken into account in a field range up to 7 T for these materials. Higher fields in the region of 50 to 100 T are needed for remarkable effects [18].

![Figure 3. Photoluminescence spectrum of the WS$_2$ monolayer sample (linear plot on the left and logarithmic plot on the right hand side) at a temperature of 2 K without applied magnetic field. The logarithmic plot provides a more distinct view of the exciton and trion peaks.](image)

J. Phys.: Condens. Matter 29 (2017) 08LT02
The energy splitting of the $\sigma^-$ and $\sigma^+$ luminescence is plotted in dependence of the applied magnetic field in figure 5. The upper graph shows the splitting for the BE transitions while the lower graph displays the splitting for the free exciton and the trion.

The Zeeman splitting is given by the slope of the linear fit by the absolute difference between $\sigma^-$ and $\sigma^+$ of the center positions of the gaussian peaks for each individual species. Accordingly, for the excitonic transition we found a splitting per Tesla of 22.79 $\mu$eV $T^{-1}$. The corresponding $g$-factor for the excitonic mode can be obtained by the equation:

$$g = \frac{2(E_+ - E_-)}{\mu_B B}.$$ 

Here, $g_{\text{exc}} = -3.94 \pm 0.1$ is in good agreement with previously reported values for WS$_2$ [18]. While preparing this manuscript, we became aware of similar measurements by Plechinger et al [28]. They measured an exciton $g$-factor of 4.3. Actually this is a surprising disagreement and the reason is not yet clear. Plechinger et al explained the difference to the expected value $g_{\text{exc}} = 4$ by extra valley moments caused by self-rotation of Bloch waves. They studied exfoliated samples.

An obvious deviation to our CVD-grown samples is different A-exciton positions. In [28] 2.096 eV have been reported what is slightly lower than the position of our sample 2.102 eV. The reason is presumably different strain since the dielectric environment is the same. It is known that strain can lead to asymmetry of masses in the conduction and valence band and subsequently to a valley contribution [29, 30].

For the trion peak, we got a total splitting of 22.51 $\mu$eV $T^{-1}$ with the resulting $g$-factor of $g_{\text{trion}} = -3.89 \pm 0.1$ very close to the free exciton value and equal within the measurement accuracy.

An identical value for excitons and trions has been reported also for the selenides [9, 10, 14, 15]. Basically a very similar or identical value can be expected for excitons and trions, since the splitting arises mainly due to the difference in the orbital magnetic moment of the initial and the final state. The spin contribution is expected to be zero, since the optical transitions take place between bands having the same spin.
It should be mentioned, that there are also reports about a slightly higher g-value [13, 14] for the trion.

It is interesting to note, that the three bound exciton states exhibit different g-values. We find a splitting of 25.04 μeV T⁻¹ for the BE1 centered at 2.035 eV which gives a g-factor of $g_{BE1} = -4.33$. This value is slightly higher than the values for the free exciton transition. The second bound-excitation emission peak (BE2) centered at 2.016 eV shows a shift of 23.02 μeV T⁻¹ yielding a g-factor of $g_{BE2} = -3.98$ in agreement with the free exciton value but the third band (BE3) centered at 1.994 eV exhibits 14.28 μeV T⁻¹ with $g_{BE3} = -2.42$. The accuracy for the estimation of the g-factors is ±0.1 in our analysis, mainly caused by the uncertainty of the gaussian peak determination. A different splitting for different sample positions, as mentioned in [13], could not be observed in our CVD grown sample. Our results strongly indicate a tendency: lower emission energies of the bound excitons are due to larger binding energies to the defect, which are most likely neutral or ionized donor or acceptor states. Larger binding energies and respective stronger localization of the excitons yield obviously smaller g-values. We ascribe these changes to different valley orbital contributions to the magnetic moments of the conduction and valence band. The simple two-band $k \cdot p$ approximation with $m_c = m_v$ does not affect the transition energies. Corrections beyond the two-band model give different effective masses and respectively different valley magnetic moments for the electrons and holes [31, 32].

4. Conclusion

To summarize, we investigated the magneto-PL of CVD grown WS₂ monolayers in magnetic fields up to 7 Tesla. In Faraday geometry, we revealed the Zeeman-splitting in polarization-sensitive spectra for five excitonic modes, the A-exciton, the trion and three bound exciton states. We determined the A-exciton g-factor to be $g_{Aexc} = -3.94 ± 0.1$, the trion g-factor to be $g_{trion} = -3.89 ± 0.1$. For the bound excitons we could determine deviations from the free exciton value, which should be caused by different effective masses of the electrons and holes due to different localization lengths.

Acknowledgments

We gratefully acknowledge financial support of the German Science Foundation (DFG) in the framework of the SFB 1083. Furthermore, supply of high-quality samples for this study by 2Dsemiconductors Inc. is acknowledged.

References

[1] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Phys. Rev. Lett. 105 136805
[2] Sie E J, McIver J W, Lee Y H, Fu L, Kong J and Gedik N 2015 Nat. Mater. 14 290–4
[3] Ugeda M M et al 2014 Nat. Mater. 13 1091–5
[4] Chernikov A, Ruppert C, Hill H M, Rigosi A F and Heinz T F 2015 Nat. Photon. 9 466–70
[5] Zhao W, Ribeiro R M, Toh M, Carvalho A, Kloc C, Neto A H C and Eda G 2013 Nano Lett. 13 5627–34
[6] He K, Kumar N, Zhao L, Wang Z, Mak K F, Zhao H and Shan J 2014 Phys. Rev. Lett. 113 026803
[7] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C Y, Galli G and Wang F 2010 Nano Lett. 10 1271–5
[8] Ellis J K, Lucero M J and Scuseria G E 2011 Appl. Phys. Lett. 99 263108
[9] Li Y et al 2014 Phys. Rev. Lett. 113 266804
[10] MacNeill D, Heikes C, Mak K F, Anderson Z, Kormányos A, Zólyomi V, Park J and Ralph D C 2015 Phys. Rev. Lett. 114 037401
[11] Smolenski T, Goryca M, Koperski M, Faugeras C, Kazimierczuk T, Bogucki A, Nogajewski K, Kossacki P and Potemski M 2016 Phys. Rev. X 6 021024
[12] Cao T, Wang G, Han W, Ye H, Zhu C, Shi J, Niu Q, Tan P, Wang E, Liu B and Feng J 2012 Nat. Commun. 3 887
[13] Aivazian G, Gong Z, Jones A M, Chu R L, Yan J, Mandrus D G, Zhang C, Cobden D, Yao W and Xu X D 2015 Nat. Phys. 11 148–52
[14] Srivastava A, Sidler M, Allain A V, Lembke D S, Kis A and Imamoglu A 2014 Nat. Phys. 11 141–7
[15] Mitoglu A, Plochocka-Maude P P, Granados del Aguila A, Christianen P C M, Deligeorgis G, Anghel S, Kulkuy L and Maude K D 2015 Nano Lett. 15 4387–92
[16] Mitoglu A A, Galkowski K, Surrence A, Kotloploski W, Dumbenco D, Kis A, Maude D K and Plochocka P 2016 Phys. Rev. B 93 165412
[17] Scrace T, Tsai Y, Barman B, Schweidenback L, Petrov A, Kioseoglou G, Zhao H, Mak K F, Zhao L, Wang Z, Zhang C, Cobden D, Yao W and Xu X D 2015 Nano Lett. 15 11304–5
[18] Stier A V, McCready K M, Jonker B T, Kono J and Crooker S A 2016 Nat. Commun. 7 1–9
[19] Wang G, Bouet L, Glavoz M M, Amand T, Ivenchenko E L, Palleau E, Maric X and Urbaszek B 2015 2D Mater. 2 034002
[20] Lee C, Yan H, Brus L E, Heinz T F, Hone J and Ryu S 2010 ACS Nano 4 6831–3
[21] Molina-Sánchez A and Wirtz L 2011 Phys. Rev. B 84 155413
[22] Plechinger G, Nagler P, Kraus J, Paradiso N, Strunk C, Schühler C and Korn T 2015 Phys. Status Solidi (RRL)—Rapid Res. Lett. 9 457–61
[23] Chemikov A, Berkelbach T C, Hill H M, Rigosi A, Li Y, Aslan O B, Reichman D R, Hybertsen M S and Heinz T F 2014 Phys. Rev. Lett. 113 076802
[24] Mitoglu A A, Plochocka-Puchalska A, Jezowski R, Asghari R and Guinea F 2015 Nano Lett. 15 4387–92
[25] Kioseoglou G, Korkusinski M, Scrace T, Hanbicki A T, Currie M, Jonker B T and Petrou A 2015 Phys. Status Solidi (RRL)—Rapid Res. Lett. 9 1–9
[26] Jones A M, Yu H, Schaibley J R, Yan J, Mandrus D G, Taniguchi T, Watanabe K, Dery H, Yao W and Xu X 2016 Nat. Phys. 12 323–7
[27] Plechinger G, Nagler P, Arora A, Schmidt R, Chemikov A, del Aguila A G, Christianen P C, Bratschitsch R, Schühler C and Korn T 2016 Nat. Commun. 7 12715
[28] Plechinger G et al 2016 Nano Lett. 16 7899–904
[29] Rostami H, Roldán R, Cappelluti E, Asgari R and Guinea F 2015 Phys. Rev. B 92 195402
[30] Scalise E, Houssa M, Pourtois G, Afnan V V and Stesmans A 2014 Physica E 56 416–21
[31] Liu G B, Shan W Y, Yao Y, Yao W and Xiao D 2013 Phys. Rev. B 88 085433
[32] Kormányos A, Zólyomi V, Drummond N D, Rakyta P, Burkard G and Fal’ko V K 2013 Phys. Rev. B 88 045416