Valley pseudospin relaxation of charged excitons in monolayer MoTe₂

T Smoleński¹,², T Kazimierczuk¹,*, M Goryca¹, K Nogajewski¹, M Potemski¹,³ and P Kossacki¹

¹ Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
² Institute for Quantum Electronics, ETH Zurich, CH-8093 Zurich, Switzerland
³ Laboratoire National des Champs Magnetiques Intenses, CNRS-UGA-UPS-INSA-EMFL, 25 rue des Martyrs, 38042 Grenoble, France

E-mail: Tomasz.Kazimierczuk@fuw.edu.pl

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Abstract

Zeeman effect induced by the magnetic field introduces a splitting between the two valleys at \( K^+ \) and \( K^- \) points of the Brillouin zone in monolayer semiconducting transition metal dichalcogenides. In consequence, the photoluminescence signal exhibits a field dependent degree of circular polarization. We present a comprehensive study of this effect in the case of a trion in monolayer MoTe₂, showing that although time integrated data allows us to deduce a \( g \)-factor of the trion state, such an analysis cannot be substantiated by the timescales revealed in the time-resolved experiments.

Keywords: valley pseudospin, monolayer MoTe₂, relaxation dynamics

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

1. Introduction

Valley degree of freedom is one of the central points in the physics of two-dimensional crystals with honeycomb lattice [1], such as, for example graphene [2] and ultrathin layers of transition metal dichalcogenides [3]. This has been first theoretically recognized [4] and then largely studied in experiments, predominantly focused on the optical properties of monolayers of semiconductor transition metal dichalcogenides (S-TMDs). Distinctly, the individual valleys at \( K^+ \) and \( K^- \) points of the Brillouin zone in S-TMD monolayers can be accessed by using light with selected \( \sigma^+ \) or \( \sigma^- \) circular polarization [5–7]. Up to date, a wide variety of valley-related phenomena has been demonstrated experimentally, including valley Zeeman effect, optical orientation of the valley pseudospin, or valley coherence [8–10].

While most of the research has been so far focused on the neutral exciton (X) due its simple electronic structure, the valley degree of freedom is an integral element of allexcitonic complexes and it is an interesting property to look over also in charged excitons (CXs). Similarly to the case of spin degree of freedom, different relaxation mechanisms for X and CX complexes may result in significantly different valley relaxation time—a quantity of paramount importance for any future applications [11, 12].

In this work we focus on the CX valley relaxation in monolayer MoTe₂. The benefit from choosing this particular system is the longer bright exciton PL decay time in comparison with other monolayer semiconductor TMDs [13, 14]. The difference in the decay constants is not qualitative, but the longer decay time facilitates investigation of the dynamics of the valley effects. Apart from this issue, the presented approach should be applicable also to other members of the monolayer semiconductor TMD family.

The main motivation behind our study is to exploit the field-induced polarization [15, 16] of the negative trion in order to assess the value of the hole \( g \)-factor in monolayer MoTe₂. The idea of such a measurement is based on the notion that the difference in trion population between the two valleys is dictated by the Boltzmann factor, which in turn depends on the value of the Zeeman splitting. In our approach the valley polarization is studied by means of time-integrated photoluminescence
(PL) spectroscopy in the magnetic field up to 10 T. Such an experiment is conducted for a range of excitation intensities, which allows us to address the issue of laser-induced heating of the sample. This kind of time-integrated investigation is additionally confronted with time-resolved data, in order to substantiate a core assumption of thermal equilibrium between trions in the two valleys.

2. Photoluminescence of monolayer MoTe$_2$

The experiments reported in this work were carried out on monolayer MoTe$_2$. The flakes were mechanically exfoliated from bulk crystals with 2H structure purchased from HQ Graphene and deposited on a piece of chemically cleaned and oxygen-plasma ashed Si substrate covered with a 90 nm-thick SiO$_2$ layer. In order to obtain large, high quality monolayers, a two-stage, tape- and polydimethylsiloxane-based exfoliation technique was used. After the exfoliation, the flakes of interest were first identified by their characteristic optical contrast and then subjected to Raman scattering and atomic force microscopy measurements to unambiguously confirm their monolayer thickness.

The optical measurements were performed in a PL setup with a spatial resolution of about 1 μm. The sample was excited non-resonantly using a femtosecond Ti: sapphire laser with repetition rate of 76 MHz. The PL signal was detected either with an InGaAs CCD camera or a streak camera with an S1 cathode for time-resolved measurements. The temperature of the sample was controlled using a bath cryostat with a variable-temperature insert. The cryostat was equipped with a superconducting magnet producing magnetic field up to 10 T in the Faraday configuration.

A representative PL spectrum of a monolayer MoTe$_2$ at $T = 10$ K is presented in figure 1(a). In accordance with earlier studies [17–19], the spectrum consists of two emission peaks, corresponding to the neutral exciton (X) and the charged exciton (CX). We corroborate this assignment with time-resolved measurements shown in figure 1(b). As in all monolayer TMDs, the neutral exciton exhibits an ultra-fast decay on the order of single picoseconds, while the trion decays by an order of magnitude slower [20, 21]. The experimentally measured lifetime of the neutral exciton of $\tau \approx 3.3$ ps only slightly exceeds the jitter of our setup ($\sigma = 2.2$ ps), consistently with the measurements reported in reference [13]. On the other hand, the decay of the charged exciton yields a decay constant of $\tau \approx 19$ ps, easily resolved by the streak camera. At longer times the CX decay profile deviates from the single exponential shape, possibly due to population conversion from the dark states, but in further considerations we will only focus on the short-lived component.

The properties discussed above correspond to the case of low-temperature limit. Upon increasing the temperature, the spectrum undergoes two distinctive changes, as shown in figure 2. First, both X and CX transitions are gradually red-shifted due to the temperature dependence of the MoTe$_2$ bandgap [17]. Secondly, the overall intensity of both emission lines diminishes. The quenching occurs at a different rate for X and CX emission, which leads to temperature-induced changes in their relative intensity. It is still under debate whether these changes reflect the mass action law [22] or rather the increasing role of phonon-trion scattering, acting as a non-radiative decay channel for the trions [21]. In order to shed more light on this issue we have performed a series of time-resolved measurements at different temperatures. The results of three such measurements are presented in figure 2(b). The data clearly shows an increase of the decay rate upon increasing the temperature. As shown in figure 2(c), with the exception of the lowest temperatures, the quenching of the PL intensity and the decrease of the CX decay time exhibit the same temperature dependence. The deviation for low temperatures might be related to the biexponential character of the decay profile, which is more pronounced in that temperature range. The dependence presented in figure 2(c) can be fit by a simple model of two competing decay channels: a temperature-independent radiative recombination and a thermally activated phonon-assisted decay:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{ph}} \exp \left(- \frac{E_{ph}}{kT} \right),$$

where $E_{ph}$ is the phonon energy. The solid line in figure 2(c) presents the result of such a fitting with $E_{ph} = 14$ meV. We note that a similar dependence was observed in monolayer MoSe$_2$ in reference [21] with $E_{ph}^{(MoSe_2)} = 33$ meV. We tentatively associate the difference between these two values with the difference in the $A_{1g}$ phonon energies in the two materials, even though there is only partial quantitative agreement in this respect ($E_{A_{1g}}^{(MoSe_2)} = 30$ meV vs $E_{A_{1g}}^{(MoTe_2)} = 21$ meV [23]).

3. Influence of the magnetic field on the charged exciton valley pseudospin relaxation

In order to study the valley-related phenomena we employed a circularly-polarized detection scheme in the PL experiment.

Figure 1. (a) Representative PL spectrum of a MoTe$_2$ monolayer featuring both X and CX optical transitions. The spectrum was measured at $T = 10$ K under pulsed, non-resonant excitation at $E \approx 1.7$ eV. (b) Time-resolved PL of X and CX. The solid lines represent mono-exponential fits to both the X decay profile and the fast and slow components of the CX decay profile. Each of the fitted profiles has been convolved with a Gaussian of standard deviation 2.2 ps corresponding to the overall temporal resolution of our experimental setup, as inferred from the width of the temporal profile of the backscattered laser light (shown for reference).
carried out in high magnetic fields [24–26].

Figure 2. (a) PL spectra of a MoTe₂ monolayer taken at different temperatures, but for fixed power and energy of the pulsed laser excitation, equal to, respectively, 0.72 mW and 1.7 eV. Solid lines represent multi-peak Gaussian fits to the measured spectra. (b) Temporal decay profiles of the CX PL acquired under the same conditions as the PL spectra in (a). Solid lines are Gaussian-convolved mono-exponential fits to the experimental data. The instrument response profile determined using the laser light backscattered from the sample surface is depicted for reference. (c) The lifetime (left axis) and PL intensity (right axis) of the CX is shown. The instrument response profile determined using the laser light backscattered from the sample surface is depicted for reference. The lifetime dependence is characterized by a mono-exponential fit to the experimental data. The instrument response profile determined using the laser light backscattered from the sample surface is depicted for reference. The lifetime dependence is characterized by a mono-exponential fit to the experimental data.

Figure 3. (a) Circular-polarization-resolved PL spectra of a MoTe₂ monolayer measured at $T = 10$ K under different magnetic fields applied perpendicularly to the monolayer plane. (b) Values of Zeeman splittings of the X and CX optical transitions determined as a function of magnetic field. Solid lines represent the linear fits to the X and CX data, which correspond to spectral $g$-factors of $g_X = -4.6$ and $g_{CX} = -3.8$, respectively.

Under such conditions we independently access excitons in the K⁺ or K⁻ valley by detecting, respectively, in the σ⁺ or σ⁻ polarization [6]. In the absence of magnetic field two valleys are degenerate, yielding identical PL signal (see figure 3(a)). Upon application of magnetic field in the Faraday geometry, the valley degeneracy is lifted, as evidenced by an increased difference between the PL spectra recorded in both polarizations. The splitting of both the X and CX line grows linearly with magnetic field with a $g$ factor of $-4.6$ and $-3.8$ respectively. These values are consistent with earlier measurements carried out in high magnetic fields [24–26].

As shown in figure 3(a), the Zeeman splitting of the X and CX lines is associated with a difference in the overall PL intensity from the two valleys. The dominance of the lower energy component clearly indicates that the effect is due to relaxation of the exciton populations from the K⁻ to the K⁺ valley. A systematic analysis of this effect is presented in figure 4.

A comparison between pairs of PL spectra in each of figures 4(a)–(c) evidences that the degree of the relaxation is lower for higher excitation power used in the experiment. Similarly, a comparison across the panels 4(a–c) reveals that the degree of the relaxation is lower for higher temperatures. The combined effect of these two factors is shown in figure 4(d). The simplest interpretation of the dependence on the excitation power is the notion that the actual temperature at the laser spot is increased by stronger excitation. In this view the degree of the relaxation at a given magnetic field is governed only by the temperature, but the temperature of the sample is accurately read only for vanishing excitation power.

For the sake of deeper analysis of the data in figure 4(d) we tentatively assume a perfect thermal equilibrium between trion populations in the two valleys. The validity of this assumption will be challenged in the next section, but it allows us to link the experimentally measured ratio of the PL signals from both valleys to the intrinsic Zeeman splitting. In particular, the Boltzmann distribution dictates that

$$\frac{I_+}{I_-} = \exp \left( \frac{-g_{CX, ini} \mu B}{kT_{eff}} \right),$$

where $I_\pm$ denotes the population of trions in the K⁺ valley, $T_{eff}$ is the effective temperature at the measured spot, and $g_{CX, ini}$ is a $g$-factor of the CX state. We note that $T_{eff}$ is the temperature of the exciton system, which in the case of optical excitation can be higher than the lattice temperature.

We emphasize that the relevant $g$-factor of the CX state in equation (2) is different than the previously discussed spectral $g$-factor $g_{CX} \approx -3.8$, as the latter one is modified by the $g$-factor of the final state for the recombination. The $g$-factor of the CX may be rather considered as a $g$-factor of a minority carrier (i.e., the hole in the case of a negatively charged trion), since the two majority carriers form a singlet pair with no magnetic response. The equation (2) can be transformed to extract the $g$-factor:

$$\frac{1}{g_{CX, ini}} \frac{T_{eff}}{T} = \frac{\mu B}{kT} \log \frac{I_-}{I_+}. \quad (3)$$

The aim of introducing here the bath temperature $T$ is to make both sides of the equation dimensionless.

Figure 5(a) shows the results of application of the formula (3) to the data from figure 4(d). In such a presentation, each data series corresponding to different cryostat temperature tends to saturate at the same level for low excitation intensity. Such a behavior is expected, as for the lowest excitation powers the $T_{eff}/T$ factor in equation (3) should converge to 1. The remaining value should correspond to the inverse of the trion state $g$-factor: $1/g_{CX, ini}$. Based on our experimental data we estimate its value as $g_{CX, ini} = -8.5 \pm 1.5$, which is marked in figure 5(a) with a light-red bar. The precision of our estimation is limited, as there is no clear-cut criterion for the saturation. Additionally, reaching the sufficiently low excitation power for the lowest bath temperature was not possible due to progressively increasing accumulation time required in the PL experiment. On the other hand, the obtained value of $-8.5$ is consistent with the expectation for the valence band $g$-factor based on a simple addition of carrier spin, orbit, and valley contributions to the Zeeman effect [27, 28]. Moreover, by repeating the same procedure for the neutral exciton PL signal we
assumption we performed time-resolved PL measurements in CX populations in the two valleys. In order to verify this, a crucial element of the analysis presented in the previous section was a premise of thermal equilibrium between the CX populations in the two valleys. In order to verify this assumption we performed time-resolved PL measurements in two circular polarizations. At first sight, the results of such an experiment (see figure 6(b)) resemble the decay shown earlier in figure 1(b). However, a closer inspection reveals that the dynamics of the signal in the two circular polarizations is not identical. In order to evidence these differences, instead of analyzing each polarization separately, we calculate at each point of time the instantaneous degree of polarization. Figures 6(c)–(e) present such data series for three different experimental conditions. Our analysis of the measured transients is based on a rate-equation model presented schematically in figure 6(a). The model assumes a single relaxation time $\tau_{\text{flip}}$ for the valley pseudo-spin. The rate of inverse transition is dictated by the Boltzmann distribution with an effective temperature $T_{\text{eff}}$. The resulting thermalization of the valley pseudo-spin is accompanied by radiative recombination from each valley. The initial populations of each valley are considered as free parameters to abstract from more complex processes occurring during an initial ultra-fast relaxation of the hot photocreated carriers. As shown with solid lines in figures 6(c)–(e), we were able to fit each of the data series using a single effective temperature and relaxation time $\tau_{\text{flip}}$. Their values are shown on top of each panel in figures 6(c)–(e). A comparison of panel (c) with (e) and panel (d) with (e) proves that both fitted parameters depend on, respectively, the bath temperature and the excitation power. Particularly important is the comparison between the fitted valley relaxation time and the previously measured CX decay time. Clearly, in all the cases shown in figures 6(c)–(e) the $\tau_{\text{flip}}$ is significantly longer than the low-temperature CX recombination time $\tau_{\text{CX}} \approx 20$ ps. It entails that the bulk of the PL is emitted before the system reaches the equilibrium between the valleys. From this point of view, the lowering of the excitation power does not improve the situation, giving no warranty that in the low power limit discussed in section 3 the polarization of the time-integrated PL signal is indeed governed by the g-factor of the initial state. Moreover, our data indicates that the disparity between the valley relaxation time and the CX recombination time is more severe at lower temperatures. It leads to a counter-intuitive conclusion that elevated temperatures can provide a better estimation of the initial state g-factor, despite a worse signal-to-noise ratio due to reduced difference between the PL signals in the two polarizations.

As evidenced by this discussion, the timescales revealed by the time-resolved measurements cannot explain why the data in figure 5 converge at plausible values of the g-factors. This
The valley polarization does not start at 0, but at some finite field-dependent value. In our analysis we have treated these g-factor values as free parameters, as they originate from the interplay between little-known ultrafast cooling processes of the photoexcited carriers and the polarization of the residual carriers. It is possible that upon lowering the excitation power these starting values are getting closer to the saturation values, effectively reducing the impact of slow rate of consecutive valley pseudospin relaxation. Unfortunately, at this point we are unable to directly verify such a scenario due to limited sensitivity of the streak camera measurements.

5. Summary

In our work we have analyzed the CX valley polarization using both time-integrated and time-resolved detection of the PL signal. In either case we observed a strong dependence of the measured polarization on the bath temperature and the excitation power. The experimental data was described using simple models accounting for both these factors, which allowed us to extract parameters such as the g-factor of a CX state or a relevant valley pseudospin relaxation rate.

The result of the time-resolved experiment clearly shown that the premise of the equilibrium between the CX populations in two valleys is of no merit. Yet, we show that analysis of the time-integrated data based on this assumption still leads to realistic value of the CX g-factor. We conclude that while such an approach inherently underestimates the Zeeman splitting, the introduced error can be mitigated by avoiding too low temperatures.

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ORCID iDs

T Smoleński https://orcid.org/0000-0002-4706-7777
T Kazimierczuk https://orcid.org/0000-0001-6545-4167
M Goryca https://orcid.org/0000-0001-7582-1880
K Nogajewski https://orcid.org/0000-0001-8839-5032
M Potemski https://orcid.org/0000-0001-8881-6618
P Kossacki https://orcid.org/0000-0002-7558-1044

References

[1] Liu Y, Gao Y, Zhang S, He J, Yu J and Liu Z 2019 Valleytronics in transition metal dichalcogenides materials Nano Res. 12 2695–711
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[3] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805
[4] Rycecz A, Tworzydlo J and Beenakker C W J 2007 Valley filter and valley valve in graphene Nat. Phys. 3 172–5
[5] Cao T et al 2012 Valley-selective circular dichroism of monolayer molybdenum disulphide Nat. Commun. 3 887
[6] Mak K F, He K, Shan J and Heinz T F 2012 Control of valley polarization in monolayer MoS2 by optical helicity Nat. Nanotechnol. 7 494–8
[7] Zeng H, Dai J, Yao W, Xiao D and Cui X 2012 Valley polarization in MoS2 monolayers by optical pumping Nat. Nanotechnol. 7 490–3
[8] Avizian G et al 2015 Magnetic control of valley pseudospin in monolayer WSe2 Nat. Nanotechnol. 8 634–8
[9] Jones A M et al 2013 Optical generation of excitonic valley coherence in monolayer WSe2 Nat. Nanotechnol. 8 634–8
[10] Smoleński T, Goryca M, Koperski M, Faugeras C, Kazimierczuk T, Bogucki A, Nogajewski K, Kossacki P and Potemski M 2016 Tuning valley polarization in a WSe2 monolayer with a tiny magnetic field Phys. Rev. X 6 021024

Figure 6. (a) Scheme of transitions between the two Zeeman-split CX valley-pseudospin states, which were included in the rate equation model of the CX pseudospin relaxation. The Zeeman splitting Δg(B) is calculated using trion state g-factor of 8.5. (b) Time-resolved CX PL decay profiles measured at T = 1.7 K, P = 0.72 mW, B = 10 T in two different circular polarizations of detection (as indicated). (c)–(e) Temporal profiles of CX PL circular-polarization degree measured under different magnetic fields and various bath temperatures T and/or excitation powers P. T = 1.7 K, P = 0.72 mW (c), T = 10 K, P = 0.36 mW (d), and T = 10 K, P = 0.72 mW (e). Solid curves in panels (b)–(e) represent fits to the experimental data with the rate-equation model described in the text.
[11] Glazov M, Ivchenko E, Wang G, Amand T, Marie X, Urbaszek B and Liu B 2015 Spin and valley dynamics of excitons in transition metal dichalcogenides Phys. Status Solidi B 252 04
[12] Yan T, Qiao X, Tan P and Zhang X 2015 Valley depolarization in monolayer WSe₂ Sci. Rep. 5 15625
[13] Robert C et al 2016 Excitonic properties of semiconducting monolayer and bilayer MoTe₂ Phys. Rev. B 94 155425
[14] Schulzeitenberg AZ and Johns JE 2020 Chemical Defects Control the Exciton Lifetime in Cvd Grown, Few-Layer MoTe₂ (Electronic Structure) Accepted
[15] Li Y et al 2014 Valley splitting and polarization by the Zeeman effect in monolayer MoSe₂ Phys. Rev. Lett. 113 266804
[16] MacNeill D, Heikes C, Mak K F, Anderson Z, Kormányos A, Zólyomi V, Park J and Ralph D C 2015 Breaking of valley degeneracy by magnetic field in monolayer MoSe₂ Phys. Rev. Lett. 114 037401
[17] Lezama I G, Arora A, Ubaldini A, Barreteau C, Giannini E, Potemski M and Morpurgo A F 2015 Indirect-to-direct band gap crossover in few-layer MoTe₂ Nano Lett. 15 2336–42
[18] Ruppert C, Aslan O B and Heinz T F 2014 Optical properties and band gap of single- and few-layer MoTe₂ crystals Nano Lett. 14 6231–6
[19] Yang J, Li T, Myint Y W, Pei J, Macdonald D, Zheng J C and Lu Y 2015 Robust excitons and trions in monolayer MoTe₂ ACS Nano 9 6603–9
[20] Wang G, Palleau E, Amand T, Tongay S, Marie X and Urbaszek B 2015 Polarization and time-resolved photoluminescence spectroscopy of excitons in MoSe₂ monolayers Appl. Phys. Lett. 106 112101
[21] Robert C et al 2016 Exciton radiative lifetime in transition metal dichalcogenide monolayers Phys. Rev. B 93 205423
[22] Ross J S et al 2013 Electrical control of neutral and charged excitons in a monolayer semiconductor Nat. Commun. 4 1473
[23] Froehlicher G, Lorchat E, Fernique F, Joshi C, Molina-Sánchez A, Wirtz L and Berciaud S 2015 Unified description of the optical phonon modes in N-layer MoTe₂ Nano Lett. 15 6481–9
[24] Goryca M et al 2019 Revealing exciton masses and dielectric properties of monolayer semiconductors with high magnetic fields Nat. Commun. 10 4172
[25] Arora A, Schmidt R, Schneider R, Molas M R, Breslavec I, Potemski M and Bratschitsch R 2016 Valley Zeeman splitting and valley polarization of neutral and charged excitons in monolayer MoTe₂ at high magnetic fields Nano Lett. 16 3624–9
[26] Arora A et al 2019 Zeeman spectroscopy of excitons and hybridization of electronic states in few-layer WSe₂, MoSe₂ and MoTe₂ 2D Mater. 6 015010
[27] Srivastava A, Sidler M, Allain A V, Lembke D S, Kis A and Imamoglu A 2015 Valley Zeeman effect in elementary optical excitations of monolayer WSe₂ Nat. Phys. 11 141–7
[28] Koperski M, Molas M R, Arora A, Nogajewski K, Bartos M, Wyzula J, Vladvkova D, Kossacki P and Potemski M 2018 Orbital, spin and valley contributions to Zeeman splitting of excitonic resonances in MoSe₂, WSe₂ and WS₂ monolayers 2D Mater. 6 015001