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Report on PhD thesis of mgr Piotr Kapuściński „Fine structure and Rydberg series of excitons in transition metal dichalcogenides”.

The thesis presented by Piotr Kapuściński investigates excitonic phenomena that occurs in semiconductor transition metal dichalcogenides such as MoS_2, $MoSe_2$, WS_2 and WSe_2 but also in novel emerging material as ReS_2. The nature of excitonic transitions has been a subject of debate for many years now therefore the experimental results presented in this thesis are timely, important and of high scientific impact.

The thesis pursued the following objectives:

- Understand the exciton fine structure in molybdenum-based monolayers, determine the value of energy splitting between bright and dark excitons and identify the dark/bright nature of MoS_2;
- Observe the Rydberg series of excitons and dark excitons in tungsten-based monolayers and rhenium disulfide;
- Induce valley polarization of trions in tungsten-based monolayers through the application of tilted magnetic fields.

The results of the investigations are described in seven chapters, in total 120 pages. The findings are supported by list of publications co-authored by Piotr Kapuściński. The end of the manuscript contains the list of literature, 220 items.

The background and state-of-the-art are introduced in the first chapter. The introduction to the physics of transition metal dichalcogenides (TMDs) is very profound, it includes both the introduction to the physics of studied phenomena (excitons, fine structure) and the structural properties of the innovative materials (the nature of transition metal dichalcogenides’s bands, symmetries and the type of expected optical transitions). Current understanding of optical properties of transition

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metal dichalcogenides is presented in very comprehensive manner and contrasted with the expectations posed for this work. As the nature of the optical transitions being fully allowed (bright states) or partially allowed (darkish/dark) has been discussed for a long time now both experimentally and theoretically, this work evidence that the current-status has to be verified again. Moreover, the novel materials, rhenium-based TMDs, with significant in-plane anisotropy are introduced and the importance of the study is explained in terms of recent achievements.

The sample preparation techniques and experimental methods are provided in the second chapter. The biggest advantage of this chapter are clear and detailed illustrations of the experimental setups. The detailed presentation of the experimental aspects of the work proves the author's meticulousness and care for the scientific correctness of the presented results.

Scientific quality of experimental data and applied methodology are further revealed in four following chapters. They presents high quality scientific data on optical properties of TMDs, focused on ground excitonic resonances (third chapter) and Rydberg series (fourth and fifth chapter for WSe_2 and ReS_2, respectively). The experimental methods consisted of the measurements of micro-photoluminescence and micro-reflectance spectra in magnetic fields in Faraday, Voigt and tilted-field geometry. Worth noticing are unique high magnetic field data, where magnetic field up to 30 T was applied. These challenging and difficult experiments allowed to determine the energy splitting between the dark and bright excitonic states and their g-factors in MoS_2 monolayer. The idea to use tilted magnetic field to probe dark excitonic states appeared to be extremely useful to observe the excited states of dark excitons. The observation of Rydberg series for bright and dark excitons in h-BN encapsulated WSe_2 allowed to determine the spin-orbit splitting of the conduction band, the parameter that has been difficult to measure in other types of experiments and doubtful in theoretical models. The same methodology was applied to determine the magneto-optical properties of highly in-plane anisotropic ReS_2 and to observe the Rydberg series. Not only two bright excitons but also two dark excitons were discovered.

Both the research procedures used in this work and the research hypotheses posed are at the highest scientific level. The experimental methods and theoretical description are accurate and allowed to get a very profound picture of the optical transitions in TMDs. Well-formulated hypothesis, also supported by theoretical

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models, concerning the brightness of the optical transitions and energy-band structure found confirmation.

Personal contribution of author and originality of the work is visible in the work on many levels. First, through very sound and convincing presentation of the results. Second, through clear and well-formulated problems with clearly articulated state-of-the-art and challenges. Third, in high quality of experimental data, where the experiments themselves were demanding (low temperatures, high magnetic field, finite size monolayers, novel materials with no in-depth literature data). Finally, the accurate conclusions that author drew from numerous experimental data.

The original achievements presented in this work are the following:
- the determination of the dark nature of the neutral exciton ground state in MoS_2 monolayers,
- value of g-factor of dark exciton in MoS_2 and $MoSe_2$ and the value of the spin-orbit splitting in conduction band of WSe_2 monolayer,
- observation of the Rydberg series and dark excitons for ReS_2 bulk crystal,
- developed method to induce valley polarization of carriers in WS_2 monolayer.

The results presented in this work are highly important for fundamental understanding of optical properties of common TMDs and emerging class of TMDs, but also for application in practical light-emitting devices based on monolayers.

I hope I'll have the opportunity to ask questions during the defense of the doctoral dissertation. It seems to me that the discussion of three following issues was rather superficial:
- I slightly miss a separate chapter on the impact of the research undertaken. This information is given in the appropriate chapters and scattered throughout the work, but a small paragraph summarizing and outlining the use of the investigated effects would be also interesting.
- I would appreciate more detailed discussion on the implications of parameter that quantifies the dimensionality in the exciton excited state spectrum introduced first in Eq. 1.9. Author introduces „lower fractional-dimensional space" that in my opinion worth more discussion. Why lower dimensional space can be fractional? Eq. 1.9 further on evolved to Eq. 4.2 with unfortunate symbol δ (as for excitonic exchange splitting defined previously) and Eq. 5.1 with symbol γ. I assume they have all the same meaning. The effective dimensionality obtained for ReS_2 is puzzling. Why for

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bulk material such as investigated ReS_2 obtained values are $\gamma = -0.03$ and $\gamma = 0.21$ for two excitonic series, respectively?

- The discussion on exciton oscillator strength and it's implication to dark-bright contribution is very brief. The definition of exciton oscillator strength is missing. The sentences (page 26) „The new higher energy eigenstate has the whole oscillator strength and is therefore named as „grey exciton", and (page 27) „[…] energy difference between bright and grey excitons, […] compensated the small oscillator strength by huge population difference favouring grey exciton" could have more explanation.

Let me now discuss the thesis quality, style and illustrations. The exceptional quality of the presentation of the scientific achievements is revealed through extremely didactic presentation and detailed information directly related to the thesis subject. The manuscript is well structures and allow the reader to appreciate all achievements in a smooth and clear manner. The introductory part followed by the sample preparation techniques and experimental details form perfect scientific basis and explain the methodology, what allow the reader to understand the next chapters. The illustrations are of high quality, the drawings are carefully prepared and the charts contain all the necessary markings. The parameters determined are clearly defined and the series of results contain clear summaries. The last chapter contains conclusions that summarize the work and lists all original findings developed within this work.

Author did not avoid few editorial mistakes:

- Linguistic errors („Coulombly bound pair" instead of „Coulomb bound pair", numbers in E-4 format instead of scientific notation 10^{-4}) and typos (multiplication sign in Eq. 17; „Broch" instead of „Bloch"; „closed to" on page 23; units separated from the numerical value in the next line of text; question mark instead of emission line notion in 5.2.1, second sentence).
- The parameter δ_0 that quantifies the excitonic exchange splitting (introduced first in chapter 1.1.2), with δ_1 and δ_2 not defined, take the form of δ in the next chapters (ex 3.2) without the clear relation between them.
- Not very fortunate sentence: „Excitons and excitonic complexes are localized [in 0D structures] and can no longer be considered carriers of energy and charge" (last sentence in 1.1.3).
- Black dots are missing in Fig. 3.2 and Fig. 3.7.

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- Fig. 3.2 is plotted for $MoSe_2$ or MoS_2?

These trivial and minor shortcomings does not change the overall very good impression that the doctoral dissertation made on me. Despite the above comments, I consider the work to be very valuable and the results obtained of high importance.

The main achievements presented in the thesis are published in three research publications in Nature Communications (2020), Physical Chemistry Chemical Physics (2020), Communication Physics (2021), additional publication will appear soon. Moreover, other achievements directly related to the subject of the thesis but not included in the manuscript are published in five other publications in Nature Communications (2019), Physical Review Letters (2019), Nanoscale (2020), Nano Letters (2021), and arXiv (2021). The three publications, where Piotr Kapuściński is the first author, prove high level of scientific maturity. Number of publications, where Piotr Kapuściński contributed to the work, demonstrate his involvement and willingness to broaden horizons.

To conclude, the manuscript presented by Piotr Kapuściński is of high quality and presents important results for the scientific community. It certainly fulfills all necessary criteria for application for a PhD degree in physics at the Wroclaw University of Science and Technology and at the University Alpes of Grenoble. I recommend distinction for this doctoral dissertation.

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