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Report on the PhD manuscript by M Piotr Kapuściński

In his PhD manuscript entitled « Fine structure and Rydberg series of excitons in transition metal dichalcogenides », Piotr Kapuściński presnts his scientific results in magneto-optical spectroscopy in the prospect of obtaining the PhD title from Wrocław University of Science and Technology and Université Grenoble Alpes. The manuscript is well written, and the scientific results are sound and novel. They have already given rise to three publications in peer-reviewed journals and a fourth paper is submitted. Piotr Kapuściński is the first author of three of these publications, and he is co-author of five other scientific papers that are not covered in his PhD manuscript, where he decided to concentrate on his main results on the excitonic spectra in two-dimensional (2D) semiconducting transition-metal dichalcogenides (S-TMD) in a strong magnetic field. Based on the impressive amount of scientific results obtained during his PhD studies and the high quality of the presented manuscript, there is no doubt that Piotr Kapuściński merits the PhD degree. I therefore strongly recommend the oral defense of his PhD thesis.

The manuscript contains seven chapters. After a short pedagogical introduction to the electronic and spectroscopic excitonic properties of 2D S-TMD (chapter 1) and to the basic samples and experimental techniques (chapter 2), Piotr Kapuściński presents his original work in chapters 3 to 6, while the last chapter is devoted to conclusions and perspectives. Chapter 3 is concerned with a determination of the energy difference between the ground states of bright and dark excitons. While the spin orientation of the valence-band electrons is fixed in each of the valleys by a prominent spin-orbit coupling, the spin-orbit coupling in the conduction band is relatively low. Since the light-matter coupling preserves the spin orientation, only electron-hole pairs with the same spin orientation are optically active (bright excitons), while excitons containing parners with opposite spin are dark. The latter can, however, be made visible by an inplane magnetic field which forces the spins to become partially parallel if the Zeeman effect is sufficiently strong with respect to the spin-orbit coupling in the conduction band (magnetic brightening). With the help of this technique, Piotr Kapuściński could show that the ground-state exciton in MoS2 contrary to the other studied S-TMD is indeed a dark exciton, and he could determine quantitatively the material-relevant parameters, such as the energy difference between the dark and the bright excitons as well as the different g-factors. Moreover, a small exchange interaction between dark excitons from different valleys splits the latter into a dark and a grey branch, albeit with a relatively small splitting (< 1meV).

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Not only the ground state dark excitons can be magnetically brightened, but also its excited states (the ns-states in analogy with the hydrogen atom). This is the subject of chapter 4, where the Rydberg series of dark excitons in WSe2 is investigated in the Voigt geometry. Most saliently, this allows for an experimental determination of the spin-orbit coupling in the conduction band, which is distinct from the energy difference between the (ground states of the) dark and bright excitons due to exchange effects and a difference in the effective masses. Piotr Kapuściński finds a value of 14 meV for the spin-orbit coupling in WSe2, while the difference in binding energy between the dark and bright exciton is found to be 28 meV. This result seems a little bit puzzeling in that a value of ~40 meV is given for the latter in table 3.1 (p.41). Is that due to a difference in the definition of the binding energy ? This point might be discussed in further detail during the oral defense.

In constrast to monolayer S-TMD, chapter 5 is concerned with the bulk TMD ReS2, which is much less studies and thus less known than the other materials (MoS2, MoSe2, WS2, WSe2,...), both from a theoretical and an experimental point of view. Piotr Kapuściński's spectroscopic results are therefore extremely useful and shed light on the excitonic properties of this material, which is furthermore characterised by a strong band anisotropy. Four Rydberg series could be classified into two families of bright and dark excitons each, and through careful inplane-field measurements and theoretical modeling, similar to that in chapter 3, Piotr Kapuściński shows convincingly that all excitons stem from the same valley. Thus a multivalley scenario that has sometimes been invoked as well as an indirect gap could be excluded. As in the previous chapters, the dark excitons were magnetically brightened by an inplane magnetic field whose orientation was also used to probe the inplane anisotropy.

The last chapter 6, before the conclusions, is concerned with charged excitons (trions) in WS2 that are spectroscopically probed in both photoluminescence and reflectivity. The WS2 representative of the 2D group-VI semiconducting TMD has been chosen for its rich reflectivity spectrum. In addition to the neutral exciton, two resonances are found in reflectivity that correspond to the spin-singlet and -triplet trions. The application of an out-of-plane magnetic field (Faraday geometry) allows one to measure the spin splittings of both trion types and thus to access the effective g-factors. Interestingly, the two techniques provide different values for the g-factors ; while those measured in photoluminescence agree are the same for the singlet and the triplet and agree with the value obtained for the neutral exciton, reflectivity provides different values. Piotr Kapuściński conjectures that this is due to charge redistribution induced by the magnetic field. However, one may ask the question why this effect provides different results for the two different techniques. Also this may be a point to be discussed during the oral defense.

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In conclusion, the manuscript is clearly written, and I appreciated the detailed physical discussions and the theoretical modeling of the measured results. The experimental results are of high quality and are important for the highly competitive community of scientists working on the spectroscopic and electronic properties of this novel class of 2D semiconductors. I therefore recommend the oral defense of Piotr Kapuściński's PhD thesis.

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