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Report on the thesis dissertation presented by Katarzyna Posmyk entitled “Determination of the Exciton Fine Structure in Two-Dimensional Metal-Halide Perovskites”

The manuscript presented by Ms. Katarzyna Posmyk is devoted to optical studies of excitonic complexes in two-dimensional (2D) hybrid lead halide perovskites. This material system has been the subject of intensive research due to its promising application potential. Despite this, several fundamental aspects related to the nature of strong optical transitions and the detailed excitonic properties remain open questions, which justifies the conducted research.

The presented studies were carried out on high-quality crystals, prepared mainly by the author, and included polarization-resolved reflectivity and photoluminescence measurements, as well as polarization-resolved experiments in high magnetic fields. The precise magneto-optical measurements enabled a convincing determination of the fine structure of the excitonic complexes in a representative 2D perovskite material — phenylethylammonium lead iodide with a single layer of octahedral units. The experimental data also allowed identification of free exciton lines in complex photoluminescence spectra.

Additionally, the excitonic properties were investigated for analogous materials containing two, three, and four layers of octahedral units, leading to interesting conclusions regarding the evolution of material parameters along the transition from the 2D limit to the bulk form.

The thesis is organized into four main chapters. The first and longest one provides background knowledge on metal-halide perovskites, including their types, chemical composition and structure, band structure, and basic information about excitons in semiconductors. The introduction to exciton physics is more elaborated and covers the fine structure of exciton and the basic concepts of how it is determined by the crystal symmetry, what are the selection rules, and how does it evolve in a magnetic field. These considerations are important for the rest of the work and directly lead to the main objectives of the thesis, which are clearly defined. The only minor shortcoming here is a brief association of the PL intensity with the oscillator strength of the dark state, without a clear statement that this holds only when nonradiative processes are much faster than radiative ones - which is usually the case for small magnetic fields when the oscillator strength of the dark state is very low.

Chapter 2 introduces the sample preparation and experimental methods used in the study. The precise and careful description of the material growth procedures is very valuable, as the preparation of high-quality crystals is crucial for observing well-resolved, narrow excitonic lines. The description of the experimental setups also demonstrates good knowledge of experimental techniques; it is comprehensive and clear. However, I find the general description of photoluminescence mechanisms and the shape of the absorption spectra somewhat oversimplified and perhaps unnecessary, since the main results of the work are discussed in much greater detail. For example, when discussing the Coulomb correction to the absorption, one might expect a mention of the Elliott absorption edge, but this omission does not affect the overall quality of the work.

Chapter 3 is devoted to the main experimental results obtained for the 2D perovskite material with monolayers of octahedral units. The optical reflectivity and photoluminescence spectra are discussed, including their evolution with excitation power and temperature. In particular, it is clearly shown that the main photoluminescence band is not related to direct recombination of free excitons. The key results are, however, obtained from polarization-resolved measurements performed in various configurations relative to the crystal planes, leading to the identification of bright excitonic states. Additional measurements in a magnetic field reveal a photoluminescence line emerging below the main band, which is associated with the dark exciton recombination. The data and analysis are clear, careful, and well presented. I have only two remarks concerning this chapter. Firstly, I do not agree that the Lorentzian shape of the photoluminescence exciton line provides sufficient grounds to claim that its width is lifetime-limited (page 56). Relatively broad lifetime-limited lines would be quite unusual for 2D systems, and this would require better justification. Secondly, I find it surprising that the dark exciton, despite its obviously long lifetime (particularly at weak magnetic fields), is observed as a free-exciton line, while the bright excitons rapidly form polarons and most of their luminescence has a polaronic character. This point would benefit from further discussion, explanation, or analysis.

Chapter 4 presents data on the evolution of excitonic properties as the number of inorganic octahedral layers increases from one to four. Both photoluminescence and reflectivity spectra are presented for samples with one, two, three, and four layers. As in the monolayer case, the photoluminescence is dominated by a strong band below the transitions due to free bright excitons. However, the energy spacing does not change monotonically with the number of layers, and the author concludes that the PL is more complex, focusing the analysis on absorption (reflectivity). I fully agree with this decision and would even add that photoluminescence is not only a convolution of the density of states and the thermal distribution of carriers (page 72), but also results from the complex dynamics of a system that is far from thermal equilibrium. The following analysis is based on polarization-resolved reflectivity data. In my opinion, the most interesting result is the variation of the fine-structure splitting constant with the number of layers. The values of this parameter were obtained from both zero-field data and analysis of spectra in a magnetic field. Both techniques yielded almost identical results, which makes the determination highly reliable. The Landé factors for excitons and the diamagnetic shifts were also determined. The analysis in this chapter is very clear and demonstrates that even for broader excitonic lines, fine-structure parameters can be precisely determined through careful analysis of polarization-resolved spectra. The only issue not fully addressed in this chapter concerns the mechanism of the strong decrease in in-plane bright exciton splitting. Is it solely due to reduced confinement as the number of layers increases, or also related to a decrease in in-plane anisotropy caused by changes in chemical composition? Answering this question would likely require additional studies, so I do not consider this as a shortcoming of the present work.

The thesis concludes with a concise summary that appropriately synthesizes the main results.

The whole manuscript is interesting and contains highly valuable experimental data. I am not in a position to assess the language quality, but I had no difficulty understanding the text. Technically, the manuscript is well organized and includes all the necessary information.

The minor remarks mentioned above do not affect my overall very positive opinion of the significance and scientific value of the presented data, their analysis, and the conclusions. I am convinced that the manuscript fully meets the requirements for a thesis submitted for the degree of Doctor of Physics.

Moreover, I am convinced that the thesis constitutes a comprehensive and well-executed study, and that the results obtained are original and of high scientific merit. In particular, the determination of the complete fine structure of the exciton represents a valuable contribution to the field of optical studies of two-dimensional perovskites. Therefore, I strongly recommend that the thesis be accepted for the award of the degree with distinction.

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