INSTYTUT FIZYKI POLSKIEJ AKADEMII NAUK

INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES

02-668 WARSZAWA, Al. LOTNIKÓW 32/46
fax: + (48-22) 843-0926; http://info.ifpan.edu.pl

dr hab. Piotr Wojnar, prof. IFPAN tel. +(48-22)-116-3202
email: wojnar@ifpan.edu.pl

Warsaw, 07.10.2025

Assessment of doctoral dissertation of M. Sc. Katarzyna Posmyk entitled "Determination of the Exciton Fine Structure in Two-Dimensional Metal-Halide Perovskites"

The dissertation of M. Sc. Katarzyna Posmyk concerns the physical properties of low dimensional structures composed of metal halide perovskites. These materials attract the research interest due to their emerging applications in the field of photovoltaics and the development of efficient light sources and detectors in the visible light spectral range. The direct band gaps of metal halide perovskites and the high defect tolerance on the optical performance imply that the application range of these materials extends the conventional semiconductors including e.g., flexible and semitransparent solar cells.

The dissertation of M. Sc. Katarzyna Posmyk is not directly application oriented, but addresses the basic physical processes responsible for the extraordinary performance of low dimensional metal halide perovskites. The physical models behind the optical properties of metal halide perovskites have generally to be significantly modified as compared to conventional semiconductors which opens novel opportunities and gives rise for intensive experimental and theoretical investigations. The dissertation is focused on the fine structure of excitons in thin metal halide perovskite layers depending on their thickness and includes the determination of respective spectral positions of optically bright vs. dark excitonic states which is crucial for the performance of the light emitting devices. The results presented in this dissertation fit, therefore, to the mainstream of the solid state physics. Moreover, they represent significant advances in this field, as will be argued in the following.

The dissertation is well organized. A clear and complete introduction into the physics of metal halide perovskites is found in chapter 1. Chapter 2 is dedicated thoroughly to the description of the experimental setups and the fabrication protocols of the investigated structures by chemical synthesis methods. It is important to note that M.Sc. Katarzyna Posmyk was responsible not only for the optical spectroscopy of two-dimensional perovskites but also partially for their fabrication by using various synthesis methods. The dissertations' objectives are clearly defined at the end of chapter 1. They include the experimental determination of the exciton fine structure from a single octahedron layer of Phenylethylammomium Lead Iodide (PEPI), a representative of two-dimensional metal halide perovskites (chapter 3). Chapter 4 is dedicated to the evolution of these properties with increasing number of octahedron layers up to the bulk limit, which corresponds to the increase of the quantum well width in the case of conventional semiconductors.

I'm impressed by the results presented in chapter 3. The experimental determination of the exciton fine structure including the energy states' ordering and the energy spacing in a single octahedron PEPI layer belongs certainly to the main results of this dissertation. The novelty of this approach relies on a comprehensive study involving polarization resolved photoluminescence and reflectance in two different experimental configurations. As result, the energy of the *out of plane* oriented excitonic state with respect to the *in plane oriented* states is determined. Subsequently, the energy of the dark exciton state is unambiguously identified after its brightening by the application of an external magnetic field. The excitonic states' ordering determined in this chapter resolves a long term controversy present in the literature. A very strong point of the research is that the measurements were repeated several times on different spatial position on the same samples and various samples fabricated by applying different protocols, which emphasizes the general nature of the presented results.

I have no doubt that, indeed, the dark exciton state related emission has been detected in an external magnetic field. The increase of the emission intensity on the magnetic field which follows quadratic dependence is a clear indication for it. The question which arises is whether the dark state energy determined directly from the photoluminescence should be additionally corrected by any other effect, such as e.g., polaron formation, similar to the case of bright excitons? A brief discussion of this point would be interesting, in my opinion. Another question concerns the presence of additional resonances in the reflectance at about 2.37eV in Figure 3.13. Why these resonances are not visible in Figure 3.8 and Figure 3.3. Both remarks should be regarded rather as a contribution to the scientific discussion and do not affect my high opinion on the presented results.

The reduction of the fine structure splitting of the bright *in plane oriented* excitons and the g-factor increase with increasing number of octahedron layers, are the most important results of chapter 4. They support definitely the conclusion that the quantum and dielectric confinements play the key role in determining both quantities and show the gradual evolution of the excitonic properties between 2D and 3D limit. My only minor remark regarding this chapter concerns Figure 4.1. The excitonic resonances are ascribed either to the resonance with the highest (n = 4, 2) or with the second highest (n = 3) energy in the reflectance spectra. Therefore, the procedure of the identification of the excitonic resonances in the reflectance spectra could be explained in a more detailed manner.

The novelty of the results presented in this dissertation is supported by the fact that they have been published in three excellent internationally recognized peer reviewed journals: *Advanced Optical Materials, Journal of the American Chemical Society* and *Journal of Physical Chemistry Letters*. Katarzyna Posmyk is the first author in these publications which highlights her significant contribution.

Summarizing, my overall evaluation of the presented dissertation is very high. It represents an original approach leading to important findings concerning excitonic properties in two dimensional metal halide perovskites. All collusions are well supported by the experimental results. Therefore, I conclude that the dissertation of Katarzyna Posmyk fulfills all the requirements posed to PhD thesis and that Katarzyna Posmyk deserves the doctor degree in the field of Natural Sciences in the discipline of Physical Sciences.

Taking into account the relevance of the excitonic states' order on the optical properties of low dimensional metal halide perovskites and the fact that the presented research has solved an important controversy regarding this issue I recommend a distinction of this dissertation.

P. Wojnar

dr hab. Piotr Wojnar, prof. IFPAN