Excitonic complexes in layered van der Waals materials

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Semiconducting transition metal dichalcogenides (S-TMDs) such as MoS2, MoSe2, WS2, or WSe2 have recently attracted a lot of attention due to their unique electronic structures and optical properties. When thinned down to a monolayer, S-TMDs transform from indirect- to direct-bandgap semiconductors and exhibit a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons, or strong photocurrent response.

In my talk I will give a concise overview on excitonic complexes apparent in S-TMD thin layers with thicknesses ranging from monolayer (1 ML) to octalayer (8 MLs) investigated using micro-photoluminescence (μ-PL) spectroscopy technique in a wide temperature range (5-300 K).

The first part of my talk will be devoted to investigation of the indirect- to direct-bandgap transformation observed in the μ-PL experiment performed on thin layers of WS2 at liquid helium temperature as the layer thickness is being reduced down to an 1 ML. I will show that the indirect-related emission shifts to lower energy with increasing the flake thickness, from ∼1.7 eV for the 2 ML flake to ∼1.4 eV for the 8 ML flake, which is a consequence of a simultaneous reduction of the fundamental bandgap.

The second part of the lecture will cover the discussion of the differences between “*bright*“ and “*darkish*” MLs. In the third part, I will demonstrate that, in S-TMDs MLs the *s*-type Rydberg series of excitonic states follow a simple energy ladder: $\varepsilon ns=-Ry*/(n+\delta)2$, The effective Rydberg energy in the formula, $Ry*$ is very close to the Rydberg energy scaled by the dielectric constant of the medium surrounding the ML and by the reduced effective electron-hole mass, whereas the ML polarizability is accounted for only by δ.

The main part of my talk will be devoted to the study of emission lines apparent in the low-temperature photoluminescence spectra of *n*-doped WS2 ML embedded in hexagonal BN layers. Results of measurements in external magnetic fields and first-principles calculations will be reviewed. It will be demonstrated that apart from the neutral exciton line, all observed emission lines are related to the negatively charged excitons. Consequently, emissions due to both the bright (singlet and triplet) and dark (spin- and momentum-forbidden) negative trions as well as the phonon replicas of the latter optically-inactive complexes are identified. The semidark trions and negative biexcitons are also distinguished. On the basis of their experimentally extracted and theoretically calculated g-factors, three distinct families of emissions are identified due to exciton complexes in WS2: bright, intravalley-, and intervalley-dark. The *g*-factors of the spin-split subbands in both the conduction and valence bands are also determined.