The balance of excitation transfer and recombination processes in MoS_2 nanotubes and flakes

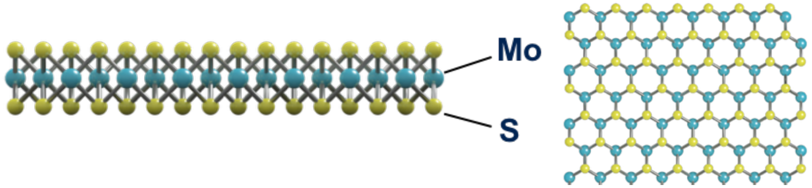
Olga Smirnova[1,2], Anna V. Rodina[2], Tatiana V. Shubina[2]

1 ITMO University, St. Petersburg 197101, Russia; 2 Ioffe Institute, St. Petersburg 194021, Russia

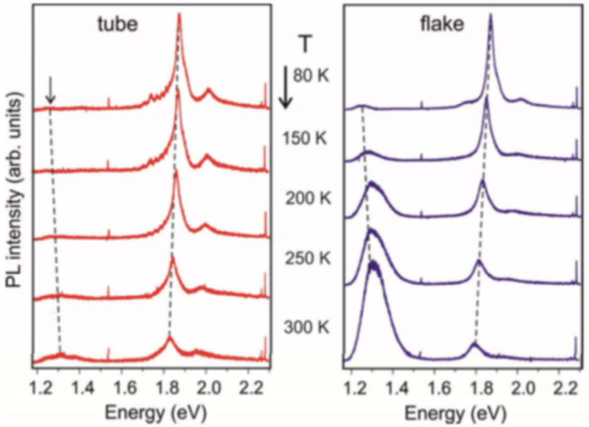
Introduction | Theory | Modeling 1 | Modeling 2 | Conclusion

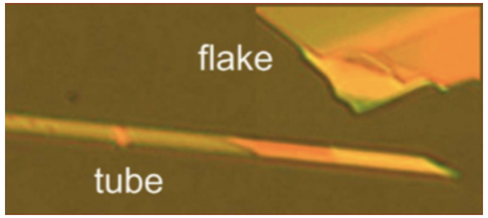
Micro-photoluminescence of MoS_2 multiwalled nanotubes and flakes, synthesized by chemical transport reaction method, were measured at the Ioffe Institute [1]. They have exhibited specific properties unexpected for multiwalled samples which have indirect band structure:

- The radiation of indirect exciton, which is energetically the lowest in multilayered structures, is absent at temperatures up to 80-100 K
- With increasing temperature, the simultaneous emission of direct and indirect excitons is observed
- In nanotubes, the direct exciton emission can dominate over the indirect exciton one in the entire temperature range

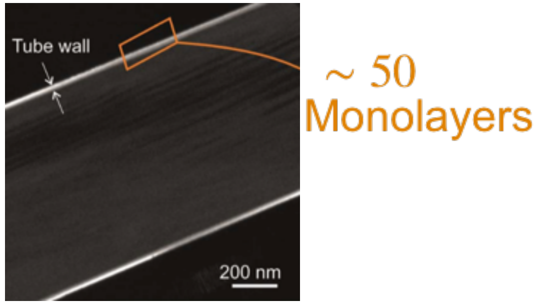


In the monolayer limit MoS_2 becomes a direct-gap semiconductor





In the 1-2 monolayer-thick flakes, the indirect emission increases in the low-temperature region and, as for the photoluminescence from direct states, drops with the increasing temperature.



Our **goal** is to propose a theoretical model that allows us to describe the experimental data for various samples and to estimate the relationship between the internal parameters for qualitatively different structures.

References

[1] Shubina T. V. et al, Annalen der Physik, 531,1800415 (2019)

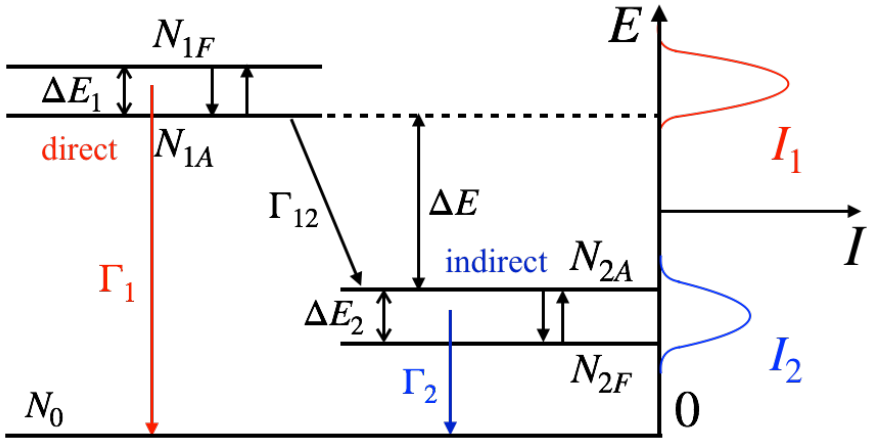
The balance of excitation transfer and recombination processes in MoS_2 nanotubes and flakes

Olga Smirnova, Anna V. Rodina, Tatiana V. Shubina

Theoretical model

The balance of the processes of transfer of excitation and recombination is considered for both direct and indirect excitonic systems, including bright (A) and dark (F) states of different nature (forbidden in spin and momentum).

We assume the lowest state of the direct exciton to be bright and vice versa for the indirect one.



The temperature dependence is given by the ratio:

$$\xi(T) = \frac{I_2(T)}{I_1(T)} = \frac{\Gamma_2^{\mathrm{rad}} N_2}{\Gamma_1^{\mathrm{rad}} N_1}$$

Mathematical description

System of rate equations:

$$\begin{cases} \dfrac{\partial N_1}{\partial t} = -(\Gamma_1 + \Gamma_{12})N_1 + G_1(t) \\[2mm] \dfrac{\partial N_2}{\partial t} = \Gamma_{12} N_1 - \Gamma_2 N_2 \end{cases}$$

We study the steady state:

$$\frac{N_2}{N_1} = \frac{\Gamma_{12}}{\Gamma_2} \longrightarrow \boxed{\xi = \frac{\Gamma_2^{\mathrm{rad}}}{\Gamma_2} \cdot \frac{\Gamma_{12}}{\Gamma_1^{\mathrm{rad}}}}$$

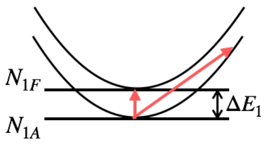
1) Sub-ensemble radiative recombination rate

$$\Gamma_i^{\mathrm{rad}} = \Gamma_{iA} \frac{N_{iA}}{N_{iA} + N_{iF}},$$

2) For the equilibrium populations (fast inner relaxation)

$$\frac{N_{1F}}{N_{1A}} = e^{-\frac{\Delta E_1}{k_B T}}, \quad \frac{N_{2F}}{N_{2A}} = e^{\frac{\Delta E_2}{k_B T}}$$

3) In addition to the main dark state, there is an ejection from the light cone



$$\frac{N_1}{N_{1A}} = 1 + e^{-\frac{\Delta E_1}{k_B T}} + f \int_{E_{\mathrm{lower}}}^{E_{\mathrm{upper}}} e^{-\frac{E}{k_B T}} dE$$

4) We assume the temperature dependent relaxation between sub-ensembles

$$\Gamma_{12} = \gamma e^{-\frac{\widetilde{\Delta E}}{k_B T}}$$

$\widetilde{\Delta E}$ - relaxation activation energy

Finally, we derive the fitting formula:

$$\boxed{\xi = \frac{d e^{-\frac{\widetilde{\Delta E}}{k_B T}}}{c} \, \frac{1 + e^{-\frac{\Delta E_1}{k_B T}} + f \int_{E_{\mathrm{lower}}}^{E_{\mathrm{upper}}} e^{-\frac{E}{k_B T}} dE}{d + 1 + e^{\frac{\Delta E_2}{k_B T}}}}$$

where $d = \dfrac{\Gamma_{2A}}{\Gamma_2^{\mathrm{nr}}}$, $c = \dfrac{\Gamma_{1A}}{\gamma}$,

$\Delta E_1, \Delta E_2$ - energy splittings in sub-ensembles

f - prefactor

The balance of excitation transfer and recombination processes in MoS_2 nanotubes and flakes

Olga Smirnova, Anna V. Rodina, Tatiana V. Shubina

Introduction | Theory | Modeling 1 | Modeling 2 | Conclusion

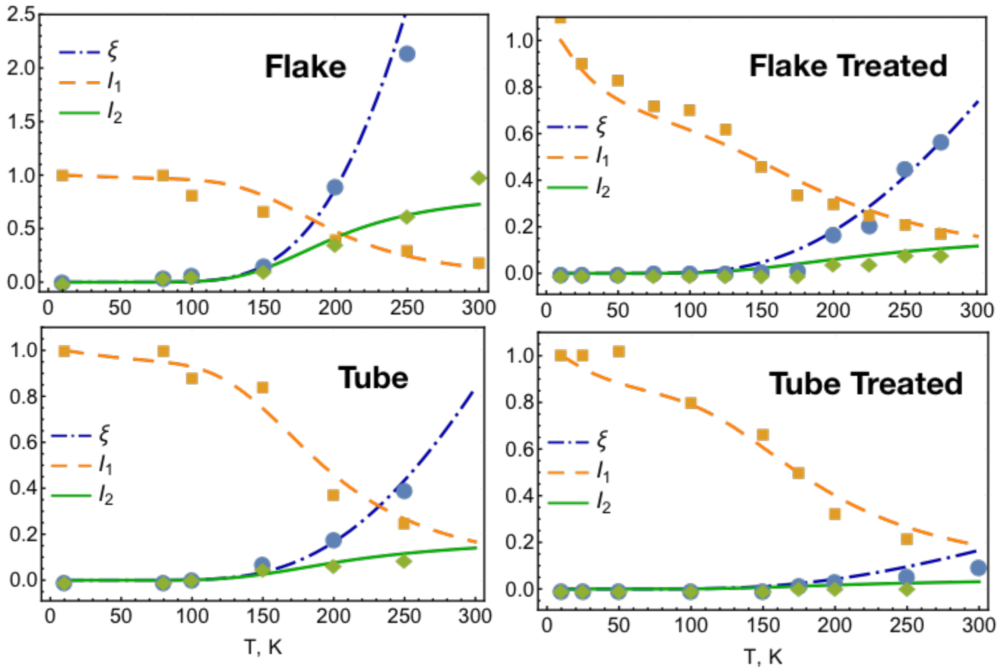
As-grown and treated samples

We studied a flake and a tube grown via the chemical transport reaction method, which then underwent the intercalation, supposedly leading to the layer separation. Fitting of the experimental dependencies measured in the as-grown and treated samples is presented in figures.

To reduce the number of parameters we make some assumptions:

- $\Delta E_1 = 3$ meV
- $E_{lower} = 0.01$
- $E_{upper} = \Delta \breve{E}$
- s (tube) = 0.2
- s (flake) = 0.02

$$s = \frac{\Gamma_{2A}}{\Gamma_{1A}}$$



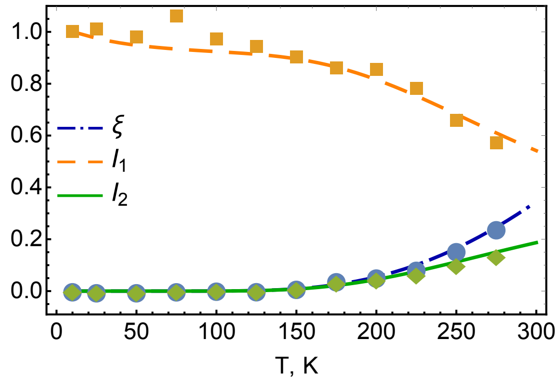
<u>Fitting parameters</u>

	c	d	f	ΔE_2	$\widetilde{\Delta E}$
Flake	0.048	11	0.2	4	80
Flake Treated	0.05	0.23	0.09	6	60
Tube	0.07	0.5	0.12	11	67
Tube Treated	0.09	0.09	0.08	11	55

- Values of ΔE_2 in all samples are of the order of 10 meV
- In treated structures the relaxation and non-radiative rates become stronger. We suppose that this is caused by the growth of the number of defects formed during intercalation

Bulk flake on a SiN_4 substrate

Thick flake on the SiN_4 substrate showed qualitatively the same dependencies



<u>Fitting parameters</u>

	c	d	f	ΔE_2	$\widetilde{\Delta E}$
bulk	0.08	1.6	0.01	5.8	90

Energy value of E_2 is of the same order as in the previous samples.

Relaxation in this sample is on the order weaker.

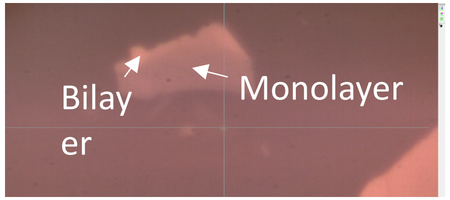
The balance of excitation transfer and recombination processes in MoS_2 nanotubes and flakes

Olga Smirnova, Anna V. Rodina, Tatiana V. Shubina

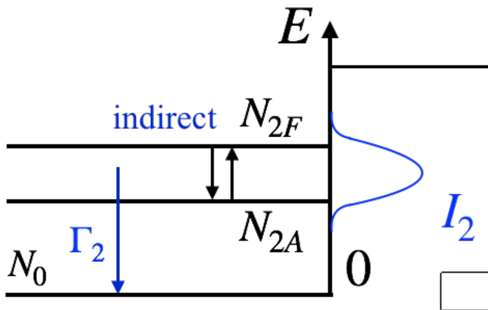
Different behavior of photoluminescence in thin flakes

In thin flakes of 1-2 monolayer thickness, another photoluminescence behavior was observed:

- At low temperatures the emission of indirect states exceeds that of the direct ones
- Both intensities drop with the increasing temperature



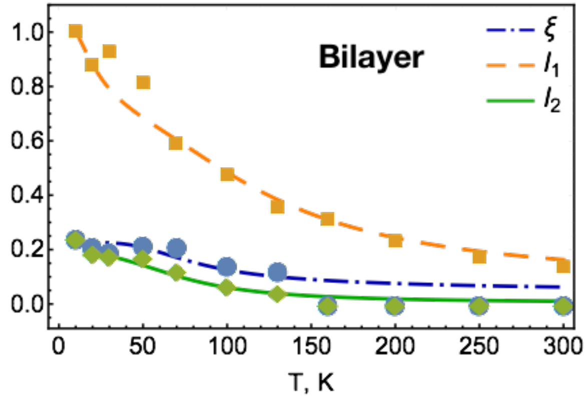
Therefore we assume the change of the level order in the subsystem of the indirect excitonic states: the lower one is bright, the upper is dark. This obliges to take into account the dark states out of the light cone in the indirect exciton subsystem.

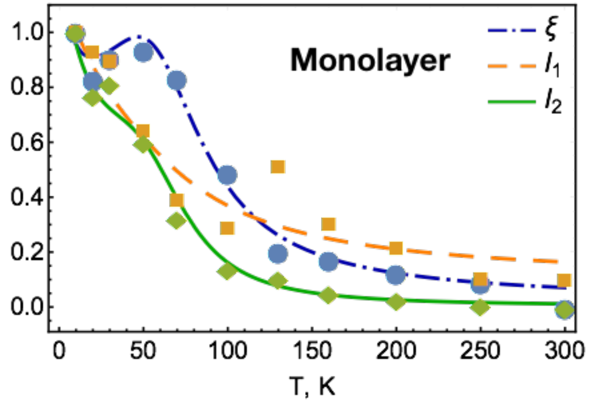


In this case the formula is modified:

$$\xi = \frac{d}{c} e^{-\frac{\widetilde{\Delta E}}{k_B T}} \frac{1 + e^{-\frac{\Delta E_1}{k_B T}} + f_1 \int dE e^{-\frac{E}{k_B T}}}{d + 1 + e^{\frac{\Delta E_2}{k_B T}} + f_2 \int dE e^{-\frac{E}{k_B T}}}$$

Also we set $\widetilde{\Delta E} = 0$ what makes relaxation temperature-independent; ΔE_1 is still 3 meV





Fitting parameters

	d	c	f_1	f_2	$E_{lower,1}$	$E_{upper,1}$	$E_{lower,2}$	$E_{upper,2}$	ΔE_2	s
Monolayer	0.017	0.015	0.49	10	10.6	30	24	100	-1.7	0.5
Bilayer	0.02	0.09	0.5	1.8	19	53	16	80	-2.5	0.28

Comparison of the obtained parameters with those of multiwalled structures indicates increase in relative radiative rate of the indirect bright state and relaxation between sub-ensembles.

The balance of excitation transfer and recombination processes in MoS_2 nanotubes and flakes

Olga Smirnova[1,2], Anna V. Rodina[2], Tatiana V. Shubina[2]

1 ITMO University, St. Petersburg 197101, Russia; 2 Ioffe Institute, St. Petersburg 194021, Russia

1. We propose a theoretical model of a complex structure of the excitonic states for explaining the temperature dependences of photoluminescence of MoS_2 flakes and tubes. The model includes bright and dark states of different nature.
2. We assume that qualitative changes in this model are possible when the thickness is going down to the monolayer limit.
3. By fitting of the experimental data with the obtained formulas for intensities, we obtain possible sets of internal parameters of the system under consideration.

In the future, we plan to increase the number of the model implementation to the experimental data and find the more or less stable ranges for the parameters.

We also intend to determine the values of the parameters from other experimental data as a photoluminescense kinetic and theoretical calculations for the studied MoS_2 structures.

Smirnova.olga248@gmail.com