Inter-valley exciton relaxation in strongly excited monolayer WSe_2

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In this work, we investigate polarization-resolved, low temperature photoluminescence (PL) of monolayer WSe_2 and show that scattering of excitons between the $+K$ and $-K$ valleys accelerates with increasing excitation power. We discuss this result within the framework of the current theory of intervalley relaxation in monolayer transition metal dichalcogenides (TMDs) — the one invoking electron-hole exchange interaction as the source of mixing of different valley states. We argue that increased excitation results in higher occupation of high kinetic energy states, giving rise to a faster inter-valley scattering.

Monolayer WSe_2 flakes were obtained by mechanical cleavage from a bulk sample grown by chemical vapor transport. The PL signal was excited by a frequency doubled output of an optical parametric oscillator (OPO) providing pulses of 300 fs duration. Time-integrated PL was detected with a nitrogen-cooled CCD camera coupled with a monochromator. Time-resolved PL was measured with a synchroscan streak camera with an overall resolution of about 5 ps. The dynamics of valley polarization is monitored via measurement of the circular polarization degree P of the PL [$P = (I^+ - I^-)/(I^+ + I^-)$, where $I^\pm$ denote PL intensities in $\sigma^\pm$ polarizations].

The PL spectrum of monolayer WSe_2 consists of peaks due to the recombination of the neutral exciton (X), charged exciton (trion, T), and emission related to localized states (L). As the excitation power is increased, the L peak saturates whereas the X intensity remains in linear regime up to highest excitation powers where heating sets in. This shows that in our experimental conditions non-linear processes such as biexciton formation or X-X annihilation are absent although at highest excitation densities average X-X distances are comparable to the X Bohr radius. PL temporal profiles for the X and T transitions both exhibit a double exponential decay. We attribute the short decay occurring with a characteristic time of $\simeq$ 10 ps to radiative recombination, while the long one with a characteristic time of $\simeq$ 50 ps to reactivation of excitons trapped on dark states. The decay times do not exhibit any excitation power dependence. Crucially, excitation with σ^+ polarized OPO beam results in $P > 0$, showing that the valley polarization survives the processes of energy relaxation, exciton formation, and recombination. Moreover, the decay time of P depends on the excitation power: decreasing from about 30 ps to 7 ps in the investigated power range. As argued in several papers, intervalley scattering occurs as a result of electron-hole exchange interaction, which acts onto the valley pseudospin as an effective in-plane magnetic field. The magnitude of this field was shown to increase with exciton kinetic energy. Thus, we attribute the increased intervalley scattering rate to increased occupation of excitonic states out of the radiative cone, where the valley states are more strongly mixed. This fraction of the exciton population undergoes a faster intervalley scattering giving rise to an increased decay of P. Our results highlight the potential of TMDs for novel valley-based devices and constitute an important contribution to the ongoing investigations of exciton dynamics in these materials.