# Spin relaxation dynamics in CdSe quantum dots doped with copper

**Ł. Kłopotowski[1], M. Szymura [1], J. Mikulski[1], P. Wojnar [1] T. Kzimierczuk [2] and J Kossut[1]**

[1] *Institute of Physics, Polish Academy of Sciences, al Lotników 32/64, 02-664 Warsaw, Poland*
[2] *Faculty of Physics, University of Warsaw, ul. Pasteura 5, 02-093 Warsaw, Poland*

Copper-doped colloidal semiconductor nanocrystals constitute a family of materials where the properties of a particular "charge transfer" (CT) exciton state can be investigated. This excited state is formed upon above band-gap photoexcitation and subsequent ultrafast capture of the hole by the Cu ion. The trapping of the hole changes the spin state of the Cu ion from a nonmagnetic $s = 0$ singlet to a $s=1/2$ doublet. Consequently, the spin properties of the electron-ion state are governed by the total spin $S=1$ or 0. Thus, Cu-doped nanocrystals offer a unique opportunity to study the spin properties of the CT exciton state composed of a delocalized electron and ion-bound hole [1].

In this work, we investigate the steady state and time-resolved photoluminescence (PL) of the copper-doped CdSe nanocrystals in a magnetic field. We address two specific issues. (i) We analyze the magnetic field dependence of the PL circular polarization. (ii) We evaluate the spin relaxation time governing the relaxation among the Zeeman split CT states.

Application of a magnetic field results in a occupation imbalance among the Zeeman split CT states giving rise to a circular polarization of the PL. This polarization is significantly stronger than for undoped CdSe nanocrystals, which we attribute to the particular spin structure of the CT state. We measure the spin relaxation time as the rise time of the PL polarization. We find that at magnetic fields below 1 T and at temperatures below 2 K, the relaxation is very slow and the relaxation time is on the order of microseconds. As the field or the temperature is increased, spin relaxation accelerates and at 8 T and 10 K, the relaxation time is on the order of 10 ns. These observations suggest a phonon-related mechanism. We argue that the relaxation involves confined acoustic phonons carrying an orbital momentum of 2 [4], in agreement with the required momentum change during relaxation between the split triplet states. To calculate the energies and the resulting PL polarization, we develop a model that accounts for the electron-ion exchange interaction, the strain in the ion vicinity, and the averaging over the nanocrystal ensemble. The model reproduces qualitatively the experimental findings and, in particular, explains the distinct nonlinearity of the polarization dependence on field observed by various authors [2-3]. We show that the effect arises as a result of different contributions to the PL polarization from nanocrystals with the quantization axis oriented parallel and perpendicular to the magnetic field.

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