Carrier-dopant exchange interactions in Mn-doped PbS colloidal quantum dots

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Carrier-dopant exchange interactions in Mn-doped PbS colloidal quantum dots were studied by circularly polarized magneto-photoluminescence. Mn substitutional doping leads to paramagnetic behavior down to 5 K. While undoped quantum dots show negative circular polarization, Mn doping changes its sign to positive. A circular polarization value of 40% was achieved at T = 7 K and B = 7 tesla. The results are interpreted in terms of Zeeman splitting of the band edge states in the presence of carrier-dopant exchange interactions that are qualitatively different from the *s,p-d* exchange interactions in II-VI systems. © *2012 American Institute of Physics*.
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In diluted magnetic semiconductors (DMS), carrier-dopant exchange interactions lead to carrier spin polarization, which can be harnessed for spintronics applications.[1] In quantum dots (QDs), confinement of carrier wave functions can profoundly modify such interactions, leading to exotic properties.[2] Colloidal QDs are of particular interest since they are free of a matrix material, provide the strongest confinement potential, and are convenient for engineering the carrier and dopant wave function overlap in core/shell heterostructures. Recently, spin properties of colloidal QDs have received significant attention. For example, Beaulac *et al.* reported light induced spontaneous magnetization up to room temperature in Mn-doped CdSe QDs;[3] Bussian *et al.* reported tunable magnetic exchange interactions in Mn-doped inverted core–shell ZnSe–CdSe nanocrystals.[4] The effective exciton *g*-factors can be tuned in both magnitude and sign, due to the interplay between quantum confinement and wave function engineering. Both Refs. 2 and 3 studied Mn-doped II-VI systems, where the well-established *s,p-d* exchange mechanism can explain the magnetooptical results.

Lead salts such as PbS belong to IV-VI narrow gap semiconductors. They have unique electronic, optical, and thermal properties with potential applications in photovoltaic, optoelectronic, and thermoelectric devices.[5–7] Different from the extensively studied II-VI systems where the band edges are located at the Γ point, the band edge states of lead salts with a rock salt structure are four-fold degenerate (eight-fold degenerate including spin) at the *L* point of the Brillouin zone.[8,9] Many of their interesting properties are associated with their small band gaps and strong spin-orbit interactions. The strong relativistic effects substantially contract the wave function of the Pb *6S* states, pushing it into the valence band, and thus the conduction band minimum (CBM) is derived mostly from the Pb *6p* states.[10] This changes the carrier-dopant exchange interactions in transition metal doped lead salts qualitatively. In addition, in QDs, quantum confinement tuning of the wave function and carrier-dopant interactions would lead to interesting magnetooptical properties. Surprisingly, while undoped IV-VI QDs have been extensively studied for their multiple exciton generation properties[11] and applications in photodetectors[12] and photovoltaics,[13] magnetooptical studies of transition metal doped IV-VI QDs are scarce in literatures.

In this paper, we report the carrier spin polarization of Mn-doped PbS colloidal QDs measured by circularly polarized magneto-photoluminescence (CP-MPL). A maximum circular polarization (*P*) value of 40% has been obtained at T = 7 K and B = 7 tesla. The sign of *P* is found to be positive, which is opposite to the sign of *P* from undoped PbS. This is attributed to the carrier-dopant exchange interactions in this system, which leads to a decrease in the effective electron *g*-factor while an increase in the hole *g*-factor, thus inverting the energy of the $\sigma+$ and $\sigma-$ transitions.

$Pb_{1-x}Mn_xS$ (x = 0.005-0.03) QDs were synthesized using the organic solution phase technique, by modifying the published procedure for undoped PbS QDs.[14] The detailed synthesis procedure will be published elsewhere. As-synthesized QDs have the rock-salt structure, as identified by the x-ray diffraction (XRD) pattern shown in Fig. 1(a). Transmission electron microscope (TEM) images (Fig. 1(b)) show that these QDs are essentially spherical, with sizes tunable from 2.5 nm to 10 nm. High resolution TEM images (Fig. 1(c)) show lattice fringes with spacings of 3.4 Å and 3.0 Å, corresponding to (111) and (200) planes of the rock-salt structure, respectively. The composition of the particles was characterized by energy dispersive x-ray spectroscopy after purifying the nanoparticles and removing the surface bound Mn^{2+} ions with pyridine. The maximum Mn^{2+} doping concentration is around 3%. Two samples: 4 nm undoped PbS QDs and 4 nm $Pb_{0.97}Mn_{0.03}S$ QDs were further investigated using magnetometry and magneto-photoluminescence spectroscopy.

Undoped PbS QDs are diamagnetic, as measured by the VSM option in a quantum design PPMS (physical property measurement system). In contrast, Mn-doped QDs give paramagnetic signals at temperatures down to 5 K (Fig. 2), indicating successful Mn incorporation. The 5 K magnetization at 9 T is about 0.55 emu/g, comparable to results in previous reports.[15] This corresponds to the Mn moment of

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