Features of spin dynamics of magnetic ions and charge carriers in self-organized quantum dots CdSe/ZnMnSe

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Abstract. Self-organized disk-shaped quantum dots of CdSe embedded in diluted magnetic ZnMnSe barrier were studied by means of pump-probe time-resolved Kerr rotation (TRKR) technique at low temperature \( T = 7 \) K. In absence of the external magnetic field TRKR signal exhibits long-living spin dynamics with the decay time exceeding the period between laser pulses. Such spin dynamics is not typical for diluted magnetic semiconductors and nano-structures based on them and could be a trace of a bound magnetic polaron. Resonant spin amplification measured in transversal magnetic field up to 1 T shows the only one peak near \( B = 0 \). In \( B = 1 \) T the long-living non-precessing signal practically vanishes, while the precessing one appears with the Larmor frequency corresponding to the Mn\(^{2+}\) ions’ net spin precession around the magnetic field. It was found that the signal consists of three components with slightly different precession frequencies that could be due to the fine structure of the manganese spin sublevels occurring because of a stress in quantum dots.

1. Introduction

In the field of modern solid state physics, phenomena based on spin-spin interactions in semiconductors are of particular interest due to their applicability in the spintronics. Ones of the systems in which such phenomena can be observed are the diluted magnetic semiconductors (DMSs) that are II-VI or III-V semiconductors where cation’s sublattice is partially substituted with magnetic transition metal ions as Mn with a half filled d-electron shell. Strong exchange interaction between charge carriers and magnetic ions leads to formation of a magnetic polaron (MP) that is a cloud of Mn\(^{2+}\) ions in a charge carrier’s localization area (electron or hole), where net magnetic moment of the former is stabilized by the effective exchange field of the latter [1]. Spin-spin interactions become more effective in systems with a quantum confinement [2] – quantum wells (QWs) or quantum dots (QDs) – that is followed by the increasing of the MP’s stabilization [3]. One of the cutting edge techniques used in study of the DMSs and nanostructures based on them is the pump-probe technique with the time resolution, which allows one to measure time-resolved dynamics of the Kerr rotation effect (TRKR).

In the present work we study the TRKR of heterostructure consisting of the CdSe QD layer embedded in lower and upper magnetic ZnMnSe barriers with thickness of 60 nm and 20 nm, respectively, pseudomorphologically grown by molecular beam epitaxy on GaAs (001) substrate.
Figure 1. PL spectra obtained from QDs at $T = 1.6$ K (black lines) and at $T = 10$ K (red lines) in $B = 0$ and $B = 6$ T in Faraday geometry under above barrier excitation ($E_{exc} = 3.06$ eV). PL data for $T = 10$ K were normalized on corresponding data for $T = 1.6$ K for the sake of clarity. Inset: PL spectra from ZnMnSe barrier at $T = 1.6$ K.

The nominal thickness of CdSe sheet is 2.8 monolayer. The sample was contained in a bath He cryostat with possibility to change a temperature from 1.6 K to 300 K and a superconducting magnet with magnetic field up to 6 T. In order to measure the TRKR signal in this sample a tunable pulsed titan sapphire laser with the repetition rate of 75.75 MHz and 1.5 ps pulse duration was used. Reflected probe beam was split into two beams with orthogonal linear polarizations by the Wollaston prism and detected by a balanced photo receiver. By means of two photo-optical modulators (PEMs) the modulation of the pump beam’s helicity at a frequency of $\nu_1 = 50$ kHz and of the probe beam’s intensity at a frequency $\nu_2 = 84$ kHz was made and a signal from the photo receiver was measured with the lock-in amplifier at a frequency of $\nu_3 = 2\nu_1 - \nu_2$. This so-called double modulation technique was carried through all measurements in order to reject a parasite constant signal in the TRKR dynamics arising from the pump beam’s light scattered on imperfect surface of the sample. Semiconductor laser with $E_{exc} = 3.06$ eV was used for photoluminescence (PL) measurement.

2. Experimental results
2.1. Photoluminescence
Black lines in the Fig. 1 show the PL spectra from QDs measured at $T = 1.6$ K in $B = 0$ and $B = 6$ T in Faraday geometry. PL from QDs is the broad band with width of about 40 meV centered at 2.31 eV that shows very small (less than 0.5 meV) Zeeman splitting in Faraday magnetic field up to 6 T. On the other hand, PL from the magnetic barrier exhibits giant Zeeman splitting of 16 meV in $B = 6$ T at $T = 1.6$ K (see inset in Fig. 1). Such a behavior of the PL is due to the fact that the magnetic ions situate only in the ZnMnSe barriers and carriers’ wavefunction, localized in the QDs, penetrates into them very little. In addition, it is seen that the PL from the QDs practically does not change its energy position at higher temperature $T = 10$ K (Red lines in the Fig. 1).

From the barrier’s PL Zeeman splitting $\Delta E$ one can estimate a manganese concentration using a formula $\Delta E = xN_0(\alpha - \beta)SB_{5/2}(S\mu g_{\text{Mn}}B/kT)$, where $x$ is a manganese concentration,
Figure 2. a) TRKR data measured at different excitation energies: upper at $E = 2.3615$ eV, lower at $E = 2.3287$ eV. Data are not shifted. b) Amplitude (red dots) and decay time (black crosses) of the TRKR signal measured at different excitation energies. Black line is PL from QDs, red line is a amplitude’s guide for the eye. $B = 0$, $P_{\text{pump}} = 3$ mW, $P_{\text{probe}} = 1$ mW. c) Pump power dependence of the TRKR’s amplitude (dots) and decay time (crosses), $B = 0$, $P_{\text{probe}} = 1$ mW at $E = 2.373$ eV. d) RSA signal measured at $\Delta t = -50$ ps (a point is shown on panel a with an arrow), $P_{\text{pump}} = 40$ mW, $P_{\text{probe}} = 1$ mW. All data measured at $T = 7$ K.

$N_0\alpha = 0.26$ eV and $N_0\beta = -1.11$ eV are electron and hole exchange constants, respectively, $S = 5/2$ is a manganese spin, $\mu$ and $k$ are Bohr magneton and Boltzmann constant, respectively, $g_{\text{Mn}} = 2$ is a manganese g-factor, $B$ is a magnetic field and $T$ is a temperature (see e.g. [1]). $B_S(x) = \frac{2S+1}{2S} \tanh(\frac{2S+1}{2S}x) - \frac{1}{2S} \tanh(\frac{1}{2S}x)$ is the Brillouin function. At $T = 1.6$ K the Brillouin function is already saturated and equal to 1 in $B = 6$ T so the manganese concentration $x$ can be estimated to be about 0.5% as $\Delta E = 16$ meV.

### 2.2. TRKR in $B = 0$ and resonant spin amplification

Dynamics of Kerr rotation signal was measured at different energies of the exciting photons at $T = 7$ K with pump beam’s power of 3 mW and probe beam’s power of 1 mW. In absence of the external magnetic field the TRKR effect manifests itself as a long-living exponentially decaying signal that has a decay time much larger than a resource of our delay line. Moreover since the signal at the negative delay time is non-zero its decay time is larger than a period between two laser pulses (13.2 ns) (Fig. 2a). As it was noted before, the modulation of either pump and probe beams will cancel out every parasite effects and the non-zero shelf at negative delay time seen in our experiment is a signal indeed. However a precise determination of the decay time of TRKR signal was out of our possibilities an estimation of it could be made if to fit the TRKR data with a following function:

$$K = A \exp(-\frac{t}{\tau}).$$

Where $A$ is the signal’s amplitude and $\tau$ is its characteristic decay time. Decay time is estimated to be $\tau \approx 15$ ns and does not depend on the excitation energy. On the other hand the dependence of TRKR signal’s amplitude on the photon energy has a resonance shape with the width about that of the PL spectrum, but with the center shifted towards shorter wavelengths on
\(\sim 40\) meV (Fig. 2b). With increasing the pump beam’s power from 3 mW to 50 mW amplitude of the signal tends to increase with further saturation. Decay time does not depend on the pump power (Fig. 2c).

In attempts of clarifying the nature of the long-living signal in the TRKR dynamics that exceeds the repetition period of our laser we used the resonant spin amplification (RSA) technique [4]. In general it consists of measuring the Kerr rotation signal at specific point of the delay line while scanning the magnetic field. That point of the delay line is usually taken to be negative – before the pump and the probe pulses coincidence (arrow in Fig. 2a) – that will ensure one that only long-living components of the signal will contribute. Fig. 2d shows the RSA signal measured at \(P_{\text{pump}} = 40\) mW and \(P_{\text{probe}} = 1\) mW at \(T = 7\) K in range of magnetic fields from -1 T to 1 T. The signal has only one peak in vicinity of \(B = 0\). Absence of other features in the RSA, namely other peaks, could be explained by several mechanisms. First of all that could mean that the long dynamics seen in TRKR signal is attributed to the magnetic moment that does not oscillate in the transversal magnetic field, but dissipates with increasing the magnetic field instead. Secondly, if that dynamics is precessing the absence of other peaks in the signal could be due to the large spread of the charge carriers’ g-factors that lead to the fast dephasing in the transversal magnetic field.

2.3. TRKR in \(B = 1\) T

Although in \(B = 1\) T the long-living component vanishes completely, another feature arises in the TRKR signal that shows an oscillatory behavior. For the analysis of the Kerr rotation dynamics we used an Eq. 1 modified on a case of oscillations:

\[
K = \sum_i A_i \exp\left(-\frac{t}{T_{2,i}}\right) \sin(2\pi \nu_{L,i} t + \phi_i). \tag{2}
\]

Where the sum is taken over several components. Here \(A_i\) is the amplitude, \(T_{2,i}\) is the dephasing time, \(\nu_{L,i}\) is the Larmor frequency and \(\phi_i\) is the initial phase of \(i\)-th component. Fitting the TRKR data with the Eq. 2 is rather complicated and consists of three components, which, however, have frequencies corresponding to the Larmor precession of the manganese ions around the external magnetic field, that is \(\nu_0 = 27.95\) GHz in \(B = 1\) T (Fig. 3). Those frequencies are close yet different from each other and from \(\nu_0\) and represent themselves as beats in the TRKR signal as seen in the inset of Fig. 3. All three components used in fit procedure are shown in the Fig. 3 as thin lines and they have many oscillation periods that allows one to define components’ parameters accurately (see Tab. 1).

| \(i\) | \(A_i\), a.u. | \(T_{2,i}\), ps | \(\nu_{L,i}\), GHz | \(\phi_i\), \(\pi\) |
|-----|------|------|--------|------|
| 1st  | 0.045 | 353  | 28.44  | 0.45 |
| 2nd  | 0.057 | 315  | 27.72  | 1.02 |
| 3rd  | 0.262 | 68   | 27.90  | 0.72 |

For all three components no parameter but the amplitude depends on an excitation energy of the photon and a pump beam’s power, and its behavior is similar to the ones obtained in absence of magnetic field.
Figure 3. TRKR data (black thick solid curve) measured at $T = 7\, \text{K}$, $B = 1\, \text{T}$, horizontal dashed line represents zero level. Red dashed curve is the fit by the Eq. 2 with three components, which are drawn as thin solid lines and shifted for clarity. Inset represents the TRKR data and the fit zoomed in to the region of farther delay times.

3. Discussion

Several candidates to have long spin dynamics observed in $B = 0$ could be named: photoexcited charge carriers, free manganese ions, and magnetic polaron. It is known that the spin lifetime of electrons and holes in diluted magnetic semiconductors (either bulk or quantum structures) is limited by units of picoseconds [5]. Secondly, manganese ions alone could be polarized by the direct exchange with photo excitons along the axis of optical excitation, and their spin could dissipate slowly because of the low spin-lattice relaxation rate. However, application of the transversal magnetic field, leading to the manganese spin precession, affects their dephasing time rather weak [6]. Therefore, since in $B = 1\, \text{T}$ manganese ions has $T_2^* \approx 300\, \text{ps}$, RSA would have had a sharp peak due to the high leap from the value of $\sim 15\, \text{ns}$. Excluding the first two candidates, we could make an assumption that the long-living dynamics of the TRKR signal could be a fingerprint of a heavy hole magnetic polaron in the system with a quantum confinement [6]. However that hypothesis should be complemented with further research on the subject.

Heavy hole’s spin is constrained along the growth axis of disc-shaped QDs due to the large spin-orbit coupling. The exchange field of the hole produced by its spin affects the magnetic ions nearby and forces them to align their magnetic moment along the growth axis as well. Such a hole magnetic polaron was observed in CdMnTe QW [6], but its stability was perturbed by a small heat (vanishes at $T = 6.3\, \text{K}$ already), whereas long-living dynamics in our system seem to be stable even at $T = 7\, \text{K}$ and high power of 40 mW. If it would be a polaron, such a high thermal stability could have been ascribed to a higher localization in all three directions in comparison to the QW. On the other hand in the CdMnTe QW polaron was observed in magnetic fields higher than 1 T that exceeds the critical magnetic field in which long dynamics in our system vanishes.

Origin of several components contributing to the TRKR signal in $B = 1\, \text{T}$ is also quite an interesting phenomenon to discuss. Beats between several components with Larmor frequencies close to each other was observed in bulk CdMnTe with very low concentration (0.1%) of Mn$^{2+}$ ions [7] and was suggested to be due to the hyperfine splitting of the spin states of manganese
ions. Since the spin of the manganese nucleus is 5/2, one should have seen 6 components, but this may not possible in our case because of an arbitrary fast decaying of the signal to the noise level. In addition to the fact that we see only three components instead of six, the Larmor frequency difference between the 1st and the 2nd components is about 700 MHz (80 neV in energy units), that is less by an order of magnitude that the constant of the hyperfine interaction (∼700 neV [8]). Other mechanism that could lead to the occuring of several manganese components in the TRKR signal is the stress of the system because of high lattice mismatch between CdSe and ZnSe. Such stress will lead the manganese spin sublevels to be split into three two-degenerate states [9]. Therefore, magnetic field motion of those states will be non-equidistant that will be followed by the presence of several frequencies in magnetic field.

The initial phase of the 1st component is close to \(\pi/2\) i.e. the corresponding ensemble of spins should start precessing from the maximum signal (projection of the magnetic moment on the \(z\) axis is non-zero at \(t = 0\)); \(\phi_{2nd} \approx \pi\), i.e. this ensemble starts its precession having a zero projection on the \(z\) axis. That is somehow counterintuitive because in the magnetic field the magnetic moment of all free manganese ensembles should be directed along \(x\) axis. Moreover the initial phase of the 3rd component neither starts with maximum signal nor with minimum, which physical meaning slips away from the understanding. Such a "strange" value of initial phase could be due to the complex process of a manganese ions precession in different magnetic field. If to assume that the heavy hole that triggers the manganese precession has a spin life time small, comparing to the \(T_2^*\) of manganese, but finite, then, for the first time, while the hole’s spin has not yet dissipated, manganese will precess in the total magnetic field \(B_{total} = B_{external} + B_{hole}\). Therefore the Larmor frequency of the manganese will be slightly higher than that given in the only external magnetic field. This frequency shift over time will lead to the "effective" shift of the initial phase, because the approximation of the TRKR signal is taken not from the \(t = 0\) but from some tens of picoseconds.

In conclusion, we have measured TRKR effect on self-organized CdSe/ZnMnSe QDs in the regime of the weak exchange interaction. In \(B = 0\) the long-living spin dynamics was observed in the TRKR signal that could be a trace of the hole magnetic polaron. However further magnetic field and temperature dependence of that long-living spin dynamics has to be measured in order to prove the hypothesis of magnetic polaron presence in that system. Several precessing components with different Larmor frequencies is seen in the TRKR signal in \(B = 1\) T that could be ascribed as an influence of the stress in the system on a manganese spin sublevels. Further determination of their origin can be done by the TRKR’s magnetic field dependence study. At higher magnetic fields (up to 6 T) beats between those components is expected to be more pronounced due to the increasing of the Larmor frequency.

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