Dynamical Spin Response in Semimagnetic Quantum Dots

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The dynamical response of a paramagnetic spin system to the exchange field of quasi-zero-dimensional electron-hole pairs in semiconductor quantum dots is investigated by time-resolved spectroscopy. The spin response time is extracted from the transient spectral shift of the photoluminescence signal caused by the dynamical spin alignment of magnetic ions incorporated in the crystal matrix. The formation of this ferromagnetically aligned spin complex is demonstrated to be surprisingly stable as compared to bulk systems, even at elevated temperatures and high external magnetic fields.

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Diluted magnetic semiconductor (DMS) quantum dots (QDs) combine the exciting electronic properties of quasi-zero-dimensional systems, where single electrons and/or holes are confined in three dimensions, with the unique giant magneto-optical effects known from diluted magnetic semiconductors, including large Faraday rotation, giant Zeeman effect, and magnetic polaron formation. In contrast to higher-dimensional systems, in a DMS QD the spin of a *single* electron, hole, or exciton interacts with the semimagnetic nanoenvironment, allowing one to study fundamental aspects of spin-spin interactions on the nanometer scale [1]. Moreover, the scattering dynamics among individual spins sets the bottom limit for the typical operation time scale of future device concepts based on a controlled interaction between carrier spins and spins of magnetic ions [2,3].

Access to the dynamical spin response in DMS QDs is provided via the formation of a quasi-zero-dimensional magnetic polaron, where the spin of an electron, a hole, or an exciton polarizes its paramagnetic environment (e.g., Mn^{2+} spins in the crystal matrix). This results in a ferromagnetically aligned spin complex, i.e., the magnetic polaron (MP). Up to now, however, the dynamics of the spin response of a paramagnetic spin system have not been studied in the exchange field of quasi-zero-dimensional carriers. Moreover, even in higher-dimensional semiconductor systems the detailed mechanism of the dynamics of Mn^{2+} spin alignment in the exchange field of excitons is still under debate, since the formation time of the magnetic polaron, τ_{MP}, usually includes both a transient change of the carrier wave function and the pure spin response time τ_S, resulting in $\tau_{\mathrm{MP}} \neq \tau_S$ [4]. These two effects cannot be separated in higher-dimensional systems, preventing direct experimental access to the spin response time τ_S.

In this Letter we present time-resolved magnetoluminescence measurements on DMS QDs that enable us to probe specifically the dynamical response of a paramagnetic spin system to the exchange field of excitons in quasi-zero-dimensional systems. Because of the strong three-dimensional confinement, the influence of a transient change of the carrier wave function during the formation process of the spin cloud can be neglected. Thus, the spin response time τ_S, becoming equal to τ_{MP}, can be extracted directly from the transient spectral shift of the photoluminescence (PL) signal of the recombining quasi-zero-dimensional electron-hole pairs. Moreover, neither increasing the temperature nor applying a magnetic field is expected to alter the excitonic wave function. This is because the sublevel splitting for self-assembled quantum dots is large as compared to kT, at least for the temperature range investigated ($T < 30$ K) [5], and because the magnetic length significantly exceeds the exciton Bohr radius even up to $B = 8$ T. This unusually favorable circumstance enables us to study systematically the dynamical response of a paramagnetic spin system to the exchange field of an electron-hole pair in a semiconductor QD.

Self-assembled semimagnetic CdSe/ZnMnSe quantum dots were grown by molecular beam epitaxy on (100) GaAs substrates. Following the deposition of the $Zn_{0.75}Mn_{0.25}Se$ barrier layer, CdSe was deposited with two nominal thicknesses, 2.0 and 2.5 monolayers (ML), respectively, ensuring three-dimensional islanding of the CdSe. Both sets of CdSe dots were then capped with a 50 nm thick $Zn_{0.75}Mn_{0.25}Se$ layer. The zero-dimensional nature of the excitons confined in the quantum dots in these samples was demonstrated using spatially resolved PL spectroscopy on individual QDs [6]. To provide a nonmagnetic reference, we also fabricated a CdSe/ZnSe QD sample grown under the same conditions, with a nominal CdSe thickness of 2.6 ML.

For the time-resolved experiments we used a tunable frequency-doubled Ti:sapphire laser generating 1.5 ps pulses with a repetition rate of 82 MHz. The transient photoluminescence signal was spectrally resolved by a 0.46 m monochromator and detected with a Streak camera followed by a Peltier-cooled charge coupled device (CCD) camera. The overall temporal resolution of the setup is about 20 ps. For measurements in a magnetic field, the samples were mounted on a cold finger in an optical He-bath cryostat equipped with a superconducting split coil magnet. For all experiments presented here we used an average excitation density below 1 $W\,cm^{-2}$ to ensure that each QD was occupied by not more than one exciton at a time. Thus a single electron-hole pair per QD is interacting with the localized Mn^{2+} spins in its vicinity.

In order to extract the spin response time of a paramagnetic spin system by using an exciton as a local probe, it is necessary to satisfy the requirement that the recombination lifetime in the system is longer than the typical time needed to align the spins in the semimagnetic environment surrounding the exciton. If that is not the case, the process of aligning the spins is interrupted by electron-hole recombination before a coherent spin cloud is formed. As was pointed out in the literature, efficient energy transfer from the exciton to the $3d$ electrons of the Mn^{2+} shell strongly reduces the excitonic lifetime, if the band gap of the DMS nanostructure is above the energy of the well-known internal Mn^{2+} transition at about 2.1 eV [7,8]. In fact, this may have been one of the major obstacles that prevented studies of exciton MP formation dynamics in self-assembled DMS QDs [9–11].

However, by a careful design of the samples, we succeeded in preparing self-assembled CdSe/ZnMnSe QDs with high quantum efficiencies, i.e., with long recombination lifetimes. This point is illustrated in Fig. 1, where the transient PL intensity is shown for two different samples. For the sample with a nominal CdSe thickness of 2.0 ML, the internal Mn^{2+} transition lies below the CdSe QD luminescence, resulting in a very rapid decay of the QD PL signal due to nonradiative losses on a time scale of 20 ps (dashed line), which is limited by our time resolution. In contrast, increasing the CdSe thickness to 2.5 ML shifts the excitonic luminescence *below* the Mn^{2+}-transition energy (see inset) yielding a high excitonic PL efficiency, with a recombination lifetime of about 580 ps [12]. This is sufficiently long to make this sample an ideal system for studying the dynamics of the spin response to the exchange field of an exciton. Note that for the entire temperature range under investigation (up to 30 K) the recombination lifetime is reduced by less than 15%, indicating only small nonradiative recombination losses.

The dynamical response of the Mn^{2+} spin system was extracted from the transient behavior of the PL emission spectrum observed after excitation with ps pulses (see Fig. 2). The excitation wavelength was 420 nm, i.e., slightly above the barrier band gap. However, it is known

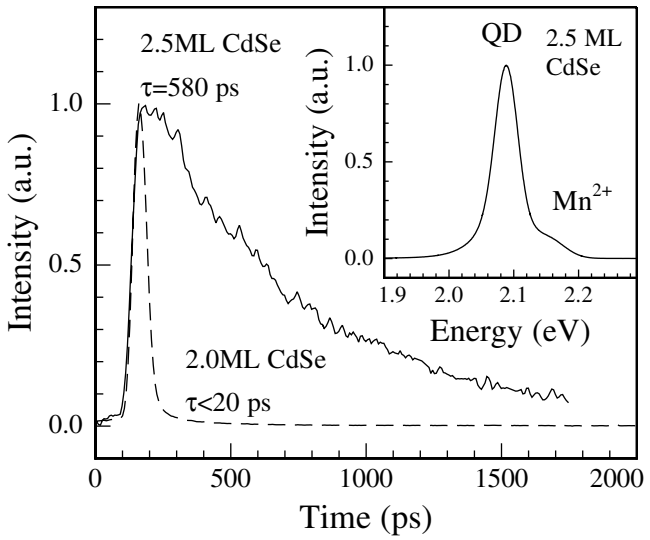

FIG. 1. Decay dynamics of the PL signal observed for semimagnetic QDs with 2.0 ML CdSe (dashed line) and 2.5 ML CdSe (solid line), respectively. For the sample with 2.0 ML CdSe a rapid quenching of the photoluminescence occurs due to a fast energy transfer into the d shell of Mn^{2+}. The inset shows a PL spectrum for the sample with 2.5 ML CdSe, where the QD emission and the internal Mn^{2+} transition are indicated.

from time-resolved measurements on single CdSe/ZnSe QDs that the carrier capture into the QD and the energy relaxation to the ground state occur on a time scale faster than our temporal resolution [13]. Thus the transient redshift of the PL signal plotted in Fig. 2 for different temperatures reflects the formation dynamics of the exciton MP, providing a spectroscopic signature of the transient ferromagnetic alignment of the Mn^{2+} spins in the exchange field of the exciton. This becomes even clearer when one investigates the equilibrium energy position E_e of the exciton MP for delay times much longer than the MP formation time: In contrast to higher-dimensional systems, an increase of the temperature does not change the electronic localization of the exciton in a QD in the temperature range under investigation, but only alters the ordering of the paramagnetic Mn^{2+} spin system [14]. Thus, the variation of E_e with temperature directly reflects the thermally induced change of the Mn^{2+} spin alignment. The temperature dependence of E_e in DMS QDs can then be well described by a Brillouin-like behavior characteristic for a paramagnetic spin system [14,15]:

$$E_e(T) = E_{\mathrm{gap}}(T) + CB_{5/2}\left(\frac{5\mu_B g_{\mathrm{Mn}} B_{\mathrm{MP}}}{2k_B(T + T_0)}\right), \quad (1)$$

where $C = -\frac{1}{2}\gamma N_0(\alpha - \beta)xS_0$ and $B_{5/2}(x)$ is the Brillouin function for spin $S = 5/2$. Here, $E_{\mathrm{gap}}(T)$ describes the temperature dependence of the band gap [16], the prefactor C depends on the well-known exchange parameters for the electron ($N_0\alpha$) and the hole ($N_0\beta$) [17], the Mn concentration x, the effective spin of the localized Mn^{2+} ions S_0, and the overlap γ of the exciton wave

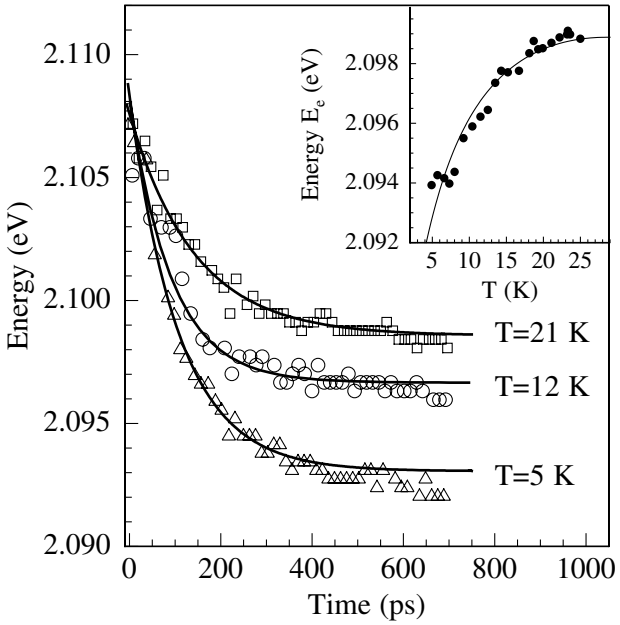

FIG. 2. Transient energy of the luminescence emission in CdSe/ZnMnSe QDs after excitation with a 2 ps laser pulse for various temperatures. Inset: Equilibrium energy position E_e at a delay time $t \gg \tau_{\mathrm{MP}}$ versus temperature. The solid line is a fit of the data according to Eq. (1).

function with the Mn^{2+} ions in the barrier. The coupled exciton-Mn^{2+} system is treated as a modified paramagnet, with an effective internal magnetic field B_{MP} describing the exchange interaction between the exciton and the Mn^{2+} spin system. The values for the effective temperature $T_0 = 3.6$ K and the effective spin $S_0 = 0.41$, which account for antiferromagnetic nearest neighbor interaction, are taken from the literature [17–19].

As shown in the inset in Fig. 2, a systematic and very pronounced increase of E_e is observed on increasing the temperature. A fit to these data according to Eq. (1) is shown in the inset as a solid line. From the fit we obtain the effective internal magnetic field $B_{\mathrm{MP}} = 2.6$ T and a corresponding overlap $\gamma = 0.07$. These results are in excellent agreement with values obtained for this sample using highly spatially resolved PL spectroscopy on single QDs [6], giving convincing evidence that the transient energy shift plotted in Fig. 2 is indeed controlled by the formation of exciton MP. For completeness we note here that in the nonmagnetic reference sample a small transient energy shift (e.g., $\approx$3 meV between $t = 0$ and $t = 200$ ps) of the PL signal is also found. However this effect, which is most likely related to a size-dependent lifetime in the dot ensemble [20], can be neglected to a first approximation, as it occurs on a time scale of 900 ps, i.e., much longer than the spin response time obtained for the semimagnetic QDs.

It is well known that the energy gain due to the formation of a MP can be described by a single exponential law [21,22]

$$E(t) = E(t = 0) - E_{\mathrm{MP}}[1 - \exp(-t/\tau_{\mathrm{MP}})], \qquad (2)$$

where $E(t)$ is the transient recombination energy, E_{MP} is the polaron binding energy (i.e., the total energy shift when equilibrium is reached, i.e., when the Mn^{2+} spins become fully aligned by the exchange field of the exciton), and τ_{MP} is the exciton MP formation time which, as was pointed out above, in this particular system corresponds to the pure spin response time τ_S.

In Fig. 3, the spin response time for the self-assembled CdSe/ZnMnSe QDs is shown as a function of temperature (circles). As the bath temperature is raised from 2 to 25 K, τ_{MP} increases from 125 to 170 ps as a consequence of competition between the exciton exchange field and thermal magnetic fluctuations that tend to suppress the MP formation. Since the MP formation time is small compared to the recombination lifetime in the whole temperature range, the entire MP formation process can thus be monitored up to the equilibrium state. For comparison, the temperature dependence of τ_{MP} for bulk $Cd_{0.75}Mn_{0.25}Se$ (dotted line) and bulk $Cd_{0.75}Mn_{0.25}Te$ (dashed line), respectively, are added in Fig. 3, as extrapolated from Zayhowski *et al.* [23].

Surprisingly, the temperature dependence of the MP formation time is considerably weaker (by about a factor of 5) than in bulk CdMnSe or bulk CdMnTe. We note here that the bulk data were obtained under similar experimental conditions (nonresonant excitation) and are therefore affected by spectral diffusion [24]. This drawback can, in principle, be eliminated using resonant excitation [24,25]. However, as was demonstrated by Itoh and Komatsu [25] for bulk $Cd_{0.8}Mn_{0.2}Te$, even in the case of resonant excitation one finds a strong increase of the MP formation time with temperature, comparable to the bulk reference data shown in Fig. 3. This demonstrates, on the one hand, the higher stability of MPs in zero dimensions, in keeping with the general trend of enhanced magneto-optical effects in semimagnetic semiconductors of reduced

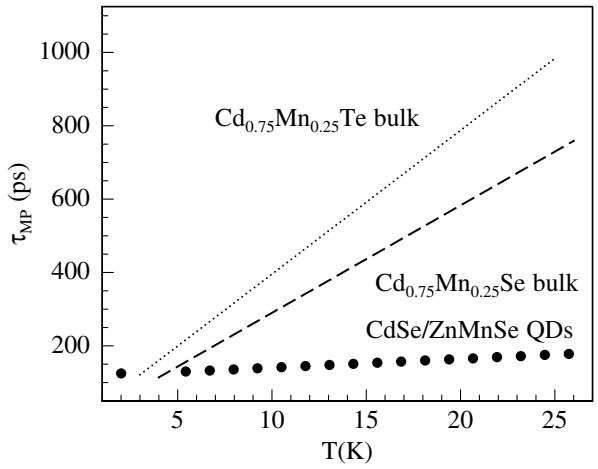

FIG. 3. Temperature dependence of the MP formation time in CdSe/ZnMnSe QDs (circles), bulk $Cd_{0.75}Mn_{0.25}Se$ (dashed line), and bulk $Cd_{0.75}Mn_{0.25}Te$ (dotted line) for different temperatures. The bulk data are taken from Ref. [23].

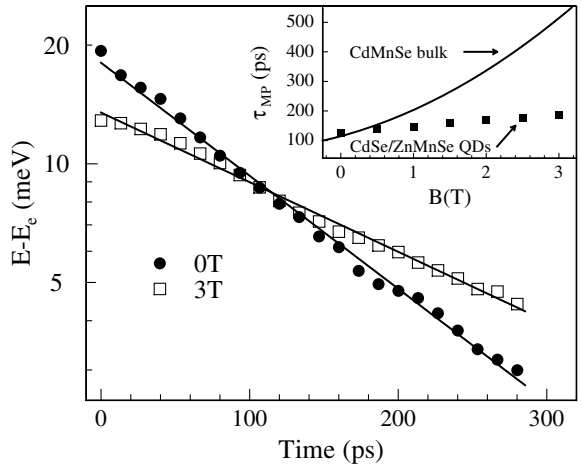

FIG. 4. Transient energy shift of the MP in CdSe/ZnMnSe QDs at zero magnetic field and at 3.0 T. Inset: Polaron formation time τ_{MP} as a function of an external magnetic field. The solid line in the inset corresponds to data for bulk $Cd_{0.75}Mn_{0.25}Se$ taken from Ref. [23].

dimensionality [26]. On the other hand, it is also important to note that in the case of quantum wells, or bulk systems, the dependence of the MP formation on temperature involves a complex interplay between transient changes of the exciton wave function, variation of the electronic localization with temperature, and spin-spin scattering, which in consequence yields $\tau_{\mathrm{MP}} \neq \tau_S$. In the case of QDs, however, the dynamics of MP formation reflects *only* the spin response time τ_S of the Mn^{2+} spins to the exchange field of the quasi-zero-dimensional exciton, i.e., $\tau_{\mathrm{MP}} = \tau_S$.

In contrast to an increase of the temperature, where the thermal energy suppresses the alignment of the Mn^{2+} spins in the exchange field of the carriers, applying an external magnetic field forces the spins of the Mn^{2+} ions to align, thus perturbing the dynamics of exciton MP formation. Figure 4 depicts in a semilogarithmic plot the transient polaronic energy shift $\Delta E = E(t) - E_e$ for different magnetic fields applied in Faraday configuration. For these experiments, a bath temperature of $T = 2$ K was used. In order to avoid saturation of the Mn^{2+} spin system, we have limited ourselves to magnetic fields below 3 T. Note, however, that even for magnetic fields up to 7 T a nonvanishing transient energy shift indicates that the zero-dimensional MP is not completely suppressed.

For the spin response time, we obtain only a slight increase from about 125 ps for $B = 0$ T to 185 ps for $B = 3$ T (see inset in Fig. 4). This is again much smaller than τ_{MP} for bulk materials [23] (see inset), where both the spin-spin interaction and the transient change of the exciton wave function control the dynamics of MP formation. We thus attribute the modest increase of the MP formation time to the magnetic field dependence of the spin response time τ_S in a semimagnetic QD.

In summary, we have used time-resolved optical spectroscopy to measure the spin response time τ_S of magnetic ions in the exciton exchange field in semimagnetic QDs. We feel that our results provide important experimental input to stimulate further theoretical work on spin-spin interaction in quasi-zero-dimensional systems. Moreover, these observations also shed valuable light on the pure spin response time τ_S of a paramagnetic system exposed to the exchange field of single carriers—a matter of considerable importance for new device concepts currently being proposed, based on the controlled spin-spin interaction in quasi-zero-dimensional (semi-)magnetic nanostructures.

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