Probing the Spin State of a Single Magnetic Ion in an Individual Quantum Dot

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The magnetic state of a *single* magnetic ion (Mn^{2+}) embedded in an individual quantum dot is optically probed using microspectroscopy. The fine structure of a confined exciton in the exchange field of a single Mn^{2+} ion ($S = 5/2$) is analyzed in detail. The exciton-Mn^{2+} exchange interaction shifts the energy of the exciton depending on the Mn^{2+} spin component and six emission lines are observed at zero magnetic field. Magneto-optic measurements reveal that the emission intensities in both circular polarizations are controlled by the Mn^{2+} spin distribution imposed by the exchange interaction with the exciton, the magnetic field, and an effective manganese temperature which depends on both the lattice temperature and the density of photocreated carriers. Under magnetic field, the electron-Mn interaction induces a mixing of the bright and dark exciton states.

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Future devices for information storage, transport, and processing are likely to be based on individual quantum objects and to involve new physical properties. They could for instance combine manipulation of charges and manipulation of spins in what is now called spintronics. Semiconductor quantum dots (QDs) hold particular promise for these future devices. Such zero-dimensional structures have been proposed as building blocks for spin-based, solid state, quantum logic gates [1–3] in a fully scalable system. Developing such devices requires, however, the ability to detect and manipulate individual spins [4,5]. Here we show how we can optically probe the magnetic state of a single Mn^{2+} ion embedded in an individual QD. The fine structure of a confined exciton in the exchange field of a single Mn^{2+} ion is analyzed in detail. At zero magnetic field, the exchange coupling with the exciton lifts the degeneracy of the six Mn^{2+} spin components. The effective spin temperature of a single Mn^{2+} ion is measured. We experimentally measure the parameters that will permit controlled manipulations of individual localized spins by single carriers.

In a diluted magnetic semiconductor, the strong *sp-d* exchange interactions between the band carriers and the transition metal ions gives rise to large magneto-optical effects [6]. In a magnetic QD, this *sp-d* interaction takes place with a single carrier or a single electron-hole pair. Recently, the formation of quasi-zero-dimensional magnetic polarons (i.e., regions with correlated carrier and magnetic ion spins) has been demonstrated [7] in individual QDs. Up to now, however, all the experimental studies on diluted magnetic QDs were focused on the interaction of a *single* carrier spin with its paramagnetic environment (*large number* of magnetic atoms). Here we reveal the various spin states of a *single* magnetic ion interacting with a *single* electron-hole pair by investigating the magneto-optic properties of an individual self-assembled QD doped with a single Mn^{2+} ion.

In the sample growth process, a low concentration of Mn is introduced into the QDs by adjusting the density of Mn atoms in the QD layer to be equal to the density of QDs ($\approx 5 \times 10^9$ cm^{-2}). The QDs are grown by molecular beam epitaxy. A $Zn_{0.94}Mn_{0.06}Te$ barrier followed by a ten monolayer ZnTe spacer is deposited on a ZnTe substrate. The CdTe QD layer is then deposited and capped with a ZnTe barrier [8]. The Mn intermixing during the growth of the ZnTe spacer introduces a sparse distribution of Mn^{2+} ions in the QD layer [9]. The photoluminescence (PL) of individual QDs is excited with the 488 nm line of

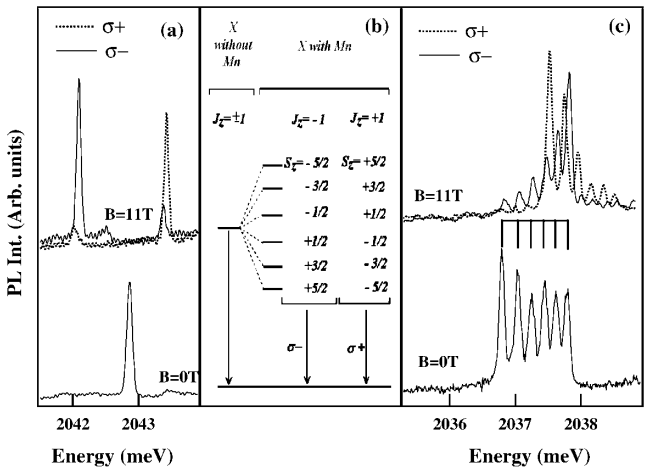

FIG. 1. Low temperature (T=5 K) PL spectra obtained at $B = 0$ T and $B = 11$ T for an individual isotropic CdTe/ZnTe QD (a) and a Mn-doped QD (c). (b) Scheme of the bright states energy levels of the Mn-exciton coupled system at zero magnetic field. The exciton-Mn^{2+} exchange interaction shifts the energy of the exciton depending on the Mn^{2+} spin projection.

an argon laser and collected through a large numerical-aperture microscope objective and aluminum shadow masks with 0.2–1.0 μm apertures. The PL is then dispersed by a 2 m additive double monochromator and detected by a nitrogen cooled Si CCD.

In Fig. 1, PL spectra of an individual Mn-doped QD are compared to those of a nonmagnetic CdTe/ZnTe reference sample. In nonmagnetic samples, narrow PL peaks (limited by the spectrometer resolution of 50 μeV) can be resolved, each attributed to the recombination of a single electron-hole pair in a single QD. Most of the individual emission peaks of magnetic single QDs are characterized by a rather large linewidth of about 0.5 meV. For some of these QDs [Fig. 1(c)], a fine structure can be resolved and six emission lines are clearly observed at zero magnetic field. The measured splitting changes from dot to dot. This fine structure splitting as well as the broadening is obviously related to the influence of the magnetic ions located within the spatial extent of the exciton wave function. The broadening previously observed in magnetic QDs has been attributed by Bacher *et al.* to the magnetic fluctuations of the spin projection of a *large number* of Mn^{2+} spins interacting with the confined exciton [7]. Here, in these low concentration Mn-doped samples, the observation of a fine structure shows that the QD exciton interacts with a single Mn^{2+} spin. In time-averaged experiments, the statistical fluctuations of a single Mn^{2+} ion ($S = 5/2$) can be described in terms of populations of its six spin states quantized along the direction normal to the QD plane. The exchange interaction of the confined exciton with the Mn^{2+} ion shifts its energy depending on the Mn^{2+} spin projection, resulting in the observation of six emission lines.

QDs with single Mn^{2+} ions were considered theoretically in the case of spherical nanocrystals with a strong confinement [10]. The eigenstates resulting from the exchange coupling of the exciton and the magnetic ion were obtained by a combination of the electron, hole, and Mn^{2+} magnetic moments. Here, in flat self-assembled QDs with a relatively weak confinement, the biaxial strains in the plane of the QD lift the degeneracy of the hole spin projections (heavy-hole/light-hole splitting). In a first approximation, our system can be described by a heavy-hole exciton in interaction with the six spin projections of the manganese ion. The spin interaction part of the Hamiltonian of this system is given by

$$H_{\text{int}} = I_e \sigma.S + I_h j.S + I_{e\text{-}h} \sigma.j \qquad (1)$$

Where I_e (I_h) is the Mn-electron (-hole) exchange integral, $I_{e\text{-}h}$ the electron-hole exchange interaction, and σ (j) the magnetic moment of the electron (hole). The initial states of the transitions are obtained from the diagonalization of the spin Hamiltonian and Zeeman Hamiltonian in the subspace of the heavy-hole exciton and Mn^{2+} spin components $|\pm 1/2\rangle_e |\pm 3/2\rangle_h |S_z\rangle_{\text{Mn}}$, with $S_z = \pm 5/2, \pm 3/2, \pm 1/2$. The final states involve only the Mn^{2+} states $|S_z\rangle_{\text{Mn}}$ with the same spin component. The resulting optical transitions are presented in Fig. 2(b). The calculation is performed with $g_e = -1.5$, $g_h = -0.1$ [11], $g_{\text{Mn}} = 2$, and $I_{e\text{-}h} = 0.66$ meV (corresponding to a singlet-triplet (ST) splitting $\hbar\omega_{\text{ST}} = 1$ meV [12]).

At zero magnetic field, the QD emission presents a fine structure composed of six doubly degenerate transitions roughly equally spaced in energy. The lower energy bright states, $|+1/2\rangle_e |-3/2\rangle_h |+5/2\rangle_{\text{Mn}}$ and $|-1/2\rangle_e |+3/2\rangle_h \times |-5/2\rangle_{\text{Mn}}$ are characterized by an antiferromagnetic coupling between the hole and the Mn^{2+} ion. The following states are associated with the Mn^{2+} spin projections $S_z = \pm 3/2, \pm 1/2$ until the higher energy states $|-1/2\rangle_e \times |+3/2\rangle_h |+5/2\rangle_{\text{Mn}}$ and $|+1/2\rangle_e |-3/2\rangle_h |-5/2\rangle_{\text{Mn}}$ corresponding to ferromagnetically coupled hole and manganese. In this simple model the zero field splitting depends only on the exchange integrals I_e and I_h, and is thus related to the position of the Mn^{2+} ion within the exciton wave function.

When an external magnetic field is applied in the Faraday geometry [Fig. 2(a)], each PL peak is further

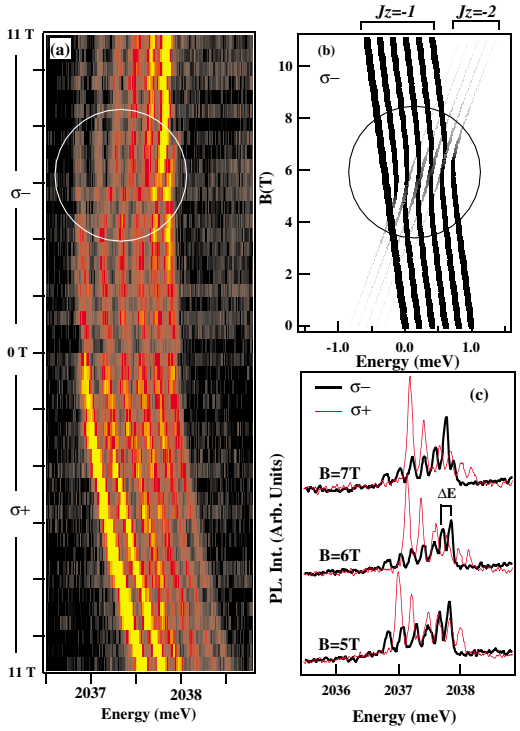

FIG. 2 (color). (a) Magnetic field dependence of the emission of a Mn-doped QD showing the anticrossing of bright and dark states around 6 T. (b) Optical transitions in $\sigma-$ polarization obtained from the diagonalization of the spin Hamiltonian and Zeeman Hamiltonian (the diamagnetic component is not included) in the subspace of the heavy-hole exciton and Mn^{2+} spin projections. The thickness of the lines is proportional to the oscillator strength of the transition. (c) Detail of the circularly polarized emission spectra around the anticrossing. Seven emission lines are resolved at $B = 6$ T in $\sigma-$ polarization.

split and 12 lines are observed, six in each circular polarization. The Zeeman effect of the Mn states is identical in the initial and the final state of the optical transitions and the six lines in a given polarization follow the Zeeman and diamagnetic shift of the exciton, as in a nonmagnetic QD. The parallel evolution of six lines is perturbed around 6 T in $\sigma-$ polarization by anticrossings observed for five of the lines. In addition, as the magnetic field increases, one line in each circular polarization increases in intensity and progressively dominates the spectrum.

The electron-Mn^{2+} part of the interaction Hamiltonian $I_e(\sigma S)$ couples the dark ($J_z = \pm 2$) and bright ($J_z = \pm 1$) heavy-hole exciton states. This coupling corresponds to a simultaneous electron and Mn^{2+} spin flip changing a bright exciton into a dark exciton. Because of the strain induced splitting of light-hole and heavy-hole levels, a similar Mn^{2+}-hole spin flip scattering is not allowed. The electron-Mn^{2+} spin flip is enhanced as the corresponding levels of bright and dark excitons are brought into coincidence by the Zeeman effect. An anticrossing is observed around 6 T for five of the bright states in $\sigma-$ polarization [experiment: Fig. 2(a) and theory: Fig. 2(b)]. It induces a transfer of oscillator strength to the dark states. In agreement with the experimental results, in the calculations the lower energy state in $\sigma-$ polarization ($|+1/2\rangle_e \times |-3/2\rangle_h |+5/2\rangle_{\mathrm{Mn}}$) does not present any anticrossing. In this spin configuration, both the electron and the Mn^{2+} ion have maximum spin projection and a spin flip is not possible.

The minimum energy splitting at the anticrossing is directly related to the electron-Mn^{2+} exchange integral I_e. For instance, the splitting measured for the higher energy line in $\sigma-$ polarization [Fig. 2(c)], $\Delta E = 150\ \mu$eV gives $I_e \approx 67\ \mu$eV. From the overall splitting measured at zero field (1.0 meV) and with this value of I_e, we obtain $I_h \approx -111\ \mu$eV. These values are in good agreement with values estimated from a modeling of the QD confinement by a square quantum well in the growth direction and a truncated parabolic potential in the QD plane. With a quantum well thickness $L_z = 3$ nm and a Gaussian wave function characterized by an in-plane localization parameter $\xi = 5$ nm we obtain $I_e \approx 65\ \mu$eV for a Mn^{2+} ion placed at the center of the QD.

However, the ratio of the exchange integral $(3I_h)/I_e \approx -5$ does not directly reflect the ratio of the *sp-d* exchange constants $\beta/\alpha \approx -4$ measured in bulk CdMnTe alloys [6]. This deviation likely comes from the difference in the electron-Mn and hole-Mn overlap expected from the difference in the electron and hole confinement length but could also be due to a change of the exchange parameters induced by the confinement [13]. A dispersion of the zero field energy splitting observed from dot to dot is then due to a variation of the Mn-exciton overlap for different QDs. However, this model does not reproduce the observed nonuniform zero field splitting [Fig. 1(c)]. A more accurate model should take into account the perturbation induced in the exciton envelope function by the exchange coupling with the magnetic ion.

As illustrated in Fig. 3(b), the relative intensities of the six emission lines observed in each circular polarization depends strongly on the applied magnetic field. The emission intensity, which is almost equally distributed over the six emission lines at zero field, is concentrated on the high energy line of the $\sigma-$ emission and on the low energy line of the $\sigma+$ emission at high magnetic field. Figure 3(b) presents the evolution with magnetic field of the emission rate of each emission line in $\sigma+$ and $\sigma-$ polarization. The emission rates follow the population of the initial states, Fig. 3(a), calculated using a Boltzmann distribution with an effective Mn temperature T_{Mn} as the only adjustable parameter [dotted lines in Fig. 3(b)]. Note that the exciton Zeeman energy and the Mn-exciton exchange energy are of opposite sign for the $\sigma+$ and $\sigma-$ emitting states and remain constant for a given polarization. As a result, the splitting between the six states emitting in a given polarization is due solely to the

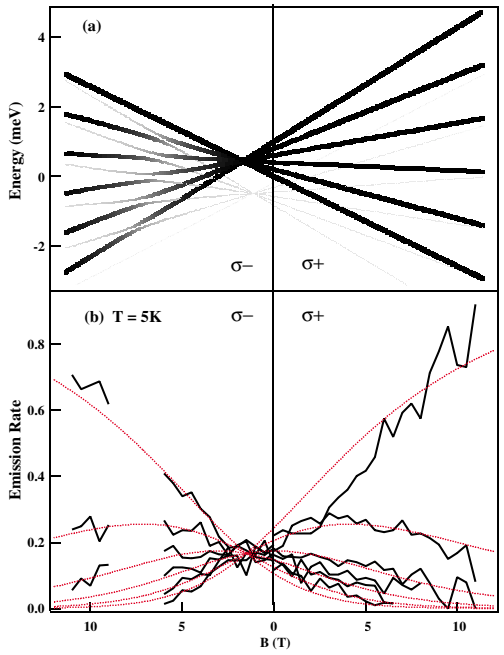

FIG. 3 (color). (a) Magnetic field dependence of the calculated energy levels of the Mn-exciton coupled system. The dark states are presented in gray. All the bright states associated with the $J_z = -1$ exciton are degenerate for an applied magnetic field of about 1.5 T. (b) Emission rate (emission intensity of each line normalized by the total integrated intensity) of the six PL lines observed in $\sigma+$ and $\sigma-$ polarization as a function of magnetic field for a fixed lattice temperature and a fixed excitation intensity. The dotted lines correspond to the Boltzmann distribution describing the thermal equilibrium of the population of the initial state (a) with an effective temperature $T_{\mathrm{Mn}} = 12$ K. For simplicity the anticrossings with the dark states are neglected in this calculation.

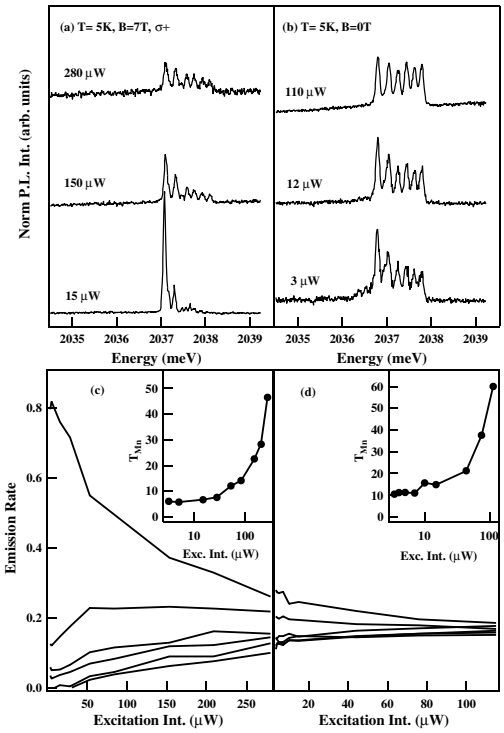

FIG. 4. (a) Normalized PL (PL spectra divided by the total integrated intensity) in $\sigma+$ polarization versus excitation intensity for a fixed temperature (5 K) and magnetic field (7 T). (b) Excitation intensity dependence of the zero magnetic field emission of a single Mn-doped QD for a fixed lattice temperature $T = 5$ K. (c), (d): extracted emission rates of each PL line as a function of the excitation intensity at 7 T (c) and 0 T (d). The inset plots the extracted Mn effective temperature.

Mn spin splitting: the sum of the Mn Zeeman splitting and the zero field Mn-exciton exchange splitting. The equilibrium position (emission rate 1/6) is then shifted by about 1.5 T to compensate for the zero field splitting induced by the exciton-Mn exchange interaction. As the magnetic field increases, the Mn^{2+} ion is progressively polarized. In time-averaged experiments, the probability to observe the recombination of the bright excitons coupled with the $S_z = -5/2$ spin projection is then enhanced. Two states dominate the spectra: $|-1/2\rangle_e \times |+3/2\rangle_h|-5/2\rangle_{\mathrm{Mn}}$ in the low energy side of the $\sigma+$ emission and $|+1/2\rangle_e|-3/2\rangle_h|-5/2\rangle_{\mathrm{Mn}}$ in the high energy side of the $\sigma-$ polarization. Changing the temperature of the Mn^{2+} ion will affect the distribution of the exciton emission intensities. The PL of the exciton is then a direct probe of the magnetic state of the Mn^{2+} ion.

The effective temperature of the manganese ion in the presence of the exciton T_{Mn} is found to depend of course on the lattice temperature but also on the laser excitation density (Fig. 4). For a fixed temperature and a fixed magnetic field, the asymmetry observed in the emission intensity distribution progressively disappears as the excitation intensity is increased [Fig. 4(a)]. The variation of T_{Mn} deduced from the emission rates, is presented in the inset of Fig. 4(c) (7 T) and Fig. 4(d) (0 T) as a function of the excitation density. A similar excitation intensity dependence of T_{Mn} was previously observed in semimagnetic quantum wells and was attributed to the heating of the Mn^{2+} ions through their spin-spin coupling with the photocreated carriers [14]. The photo carriers have excess energy. Via spin-flip exchange scattering they pass their energy to the Mn^{2+} ions and elevate their spin temperature. The energy flux from the Mn to the lattice, determined by the spin lattice relaxation, will tend to dissipate this excess energy. Under steady-state photoexcitation, the resulting temperature of the magnetic ions T_{Mn} exceeds the lattice temperature. The effect of this spin-spin coupling is strongly enhanced in our system since the isolated Mn^{2+} ion is weakly coupled to the lattice and consequently hardly thermalized with the phonon bath [15]. Resonant excitation of electron-hole pairs directly in the QD should avoid this heating.

Finally, one should notice that the exciton is more than a probe, it also changes the spin distribution of the magnetic ion. As illustrated in Fig. 4(b), at 0 T and at low excitation intensity, an asymmetry is observed in the emission intensity distribution. This polarization shows that a spin flip of the exciton-Mn system can occur during the lifetime of the exciton. As shown in Fig. 3(a), the exchange interaction with the exciton acts as an effective magnetic field which splits the Mn^{2+} levels in zero applied field, allowing a progressive polarization of its spin distribution. More generally, the interaction between the magnetic ion and the carriers (or exciton) in the QD could be exploited to manipulate the quantum state of an individual spin by optical or electrical injection of polarized carriers. Coherent manipulation of the spin state of a single magnetic ion could also be performed under pulsed resonant optical excitation, suggesting implementation of controlled spin-qubit operations.

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