

Optically Probing the Fine Structure of a Single Mn Atom in an InAs Quantum Dot

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We report on the optical spectroscopy of a single InAs/GaAs quantum dot doped with a single Mn atom in a longitudinal magnetic field of a few Tesla. Our findings show that the Mn impurity is a neutral acceptor state A^0 whose effective spin $J = 1$ is significantly perturbed by the quantum dot potential and its associated strain field. The spin interaction with photocarriers injected in the quantum dot is shown to be ferromagnetic for holes, with an effective coupling constant of a few hundreds of μeV , but vanishingly small for electrons.

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The spin state of a single magnetic impurity could be envisaged as a primary building block of a nanoscopic spin-based device [1,2] in particular for the realization of quantum bits [3]. However, probing and manipulating such a system requires extremely high sensitivity. Several techniques have been successfully developed over the past few years to address a single or few coupled spins: electrical detection [4,5], scanning tunneling microscopy (STM) [6–9], magnetic resonance force microscopy [10], and optical spectroscopy [11]. Recently, Besombes *et al.* [12,13] and Léger *et al.* [14,15] have investigated the spin state of a single Mn^{+2} ion embedded in a single II–VI self-assembled quantum dot (QD). In this system the magnetic impurity is an isoelectronic center in a $3d^5$ configuration with spin $S = 5/2$. The large exchange interaction between the spin of the photogenerated carriers confined inside the dot and the Mn magnetic moment induces strong modifications of the QD photoluminescence (PL) spectrum: $2S + 1 = 6$ discrete lines are observed, reflecting the Mn spin state at the instant when the exciton recombines.

The case of the Mn ion is different in GaAs, since the impurity is an acceptor in this matrix with a rather large activation energy (113 meV). Two types of Mn centers exist in GaAs, the A^0 and the A^- states. In low doped GaAs (below 10^{19} cm^{-2}), the former is dominant. It corresponds to the $3d^5 + h$ configuration, where h is a hole bound to the Mn ion with a Bohr radius around 1 nm [16]. When considering a single Mn impurity in InAs QD several issues arise: the impurity configuration, its possible change when photocarriers are captured, the influence on the binding energy of excitonic complexes, and the strength and sign of the effective exchange interaction with each of the carriers (electron or hole) in the QD S shell. In this Letter, we report the first evidences of a single Mn impurity in an individual InAs QD which enables us to answer most of the above questions. In particular, we find that the formation of excitons, biexciton, and trions is weakly perturbed by the impurity center, whereas the effective exchange coupling with the Mn impurity (found in the

A^0 configuration) is ferromagnetic (FM) for holes (a few $100 \mu\text{eV}$) and almost zero for the electrons.

The sample was grown by molecular beam epitaxy on a semi-insulating GaAs [001] substrate. The Mn-doped quantum layer was embedded in between an electron reservoir and a Schottky gate. This design gave us the possibility to observe both neutral and charged excitons. It consists of a 200 nm thick n -doped GaAs layer ($n = 2 \times 10^{18} \text{ cm}^{-2}$) followed by a nonintentionally doped (n - i - d) 20 nm GaAs layer, the Mn-doped QD layer, and capped with a n - i - d GaAs(30 nm)/ $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ (100 nm)/GaAs(20 nm) structure. The QD layer was formed by the deposition of 1.7 ML of InAs during 5 s. The substrate temperature was set to 500°C (optimal for QD) during the growth of the whole structure. The Mn doping was carried out by opening the Mn cell shutter during the QD growth. The cell temperature was set to 590°C . The precise determination of the Mn atom density is difficult in this material because of the large segregation of Mn atoms at these growth temperatures as observed by STM [17]. Estimations from Hall effect measurements in thick and uniformly Mn-doped GaAs layers grown at the same temperature yielded a density of approximately $1\text{--}2 \times 10^{11}$ Mn atoms per cm^2 , giving a probability of $1/3\text{--}2/3$ Mn per dot. However, in μ -PL measurements on a large collection of single QDs we observed only rare occurrences of Mn doping ($<0.1\%$), likely due to the Mn segregation away from the QD layer. Samples grown at higher Mn cell temperature (660°C) showed a much larger probability ($\sim 1\%$) of finding dots containing a single Mn atom.

The μ -PL spectroscopy of individual InAs:Mn QDs was carried out with a split-coil magneto-optic cryostat. A 2 mm focal length aspheric lens (N.A. 0.5) was used to focus the He-Ne excitation beam and to collect the PL from the sample, while the relative positioning in all three directions was ensured by AttocubeTM piezomotors. All measurements presented in this Letter were performed at low temperature ($T = 2 \text{ K}$) and the magnetic field was applied parallel to the optical axis (Faraday configuration). The PL was dispersed by a 0.6 m-focal length double

spectrometer and detected by a Nitrogen-cooled CCD array camera.

We first present the optical signature in zero magnetic field of a single Mn atom uncovered by our experiments in the PL spectrum of about 10 different QDs. A characteristic spectrum is shown in Fig. 1(a). It consists of two bright doublets labeled FM and AFM separated by an energy Δ of the order of a few 100 μeV , and of a weaker central line denoted by O. The splitting δ of the doublets is the same for both lines FM and AFM and typically amounts to a few tens of μeV .

A simple interpretation of this spectral feature can be constructed by assuming that the QD contains a Mn impurity in the A^0 configuration, i.e., a hole bound to an A^- center [16,18,19]. This acceptor state is characterized in bulk GaAs by an antiferromagnetic (AFM) “ p - d ” exchange between the $3d^5$ Mn spin $S = 5/2$ and the hole spin $J_h = 3/2$. The latter takes the form of a Heisenberg Hamiltonian $\varepsilon \hat{S} \cdot \hat{J}_h$ [18] (with $\varepsilon \sim 5$ meV), giving rise to splittings of A^0 eigenstates as a function of the total angular momentum $\hat{J} = \hat{J}_h + \hat{S}$: the triplet ground state $J = 1$ ($J_z = \pm 1, 0$) turns out to be well separated from the higher levels $J = 2, 3, 4$ by at least $2\varepsilon \sim 10$ meV. Therefore, at low temperature when $k_B T \ll 2\varepsilon$ the Mn impurity is completely thermalized in its ground state. Assuming similar p - d exchange in InAs QDs, we may consider that the photocarriers captured by the QD interact with an effective spin $J = 1$. Such a situation is depicted in Fig. 1(b) in the case of an electron-hole pair (or neutral exciton X^0) in its ground state. We focus here only on the excitonic bright states with projection of angular momentum $J_z^{\text{exc}} = \pm 1$, since the dark states ($J_z^{\text{exc}} = \pm 2$) do not contribute to the PL signal. A natural basis to describe the $A^0 + X^0$ initial states of the excitonic transition reads thus $|J_z, J_z^{\text{exc}}\rangle$. In

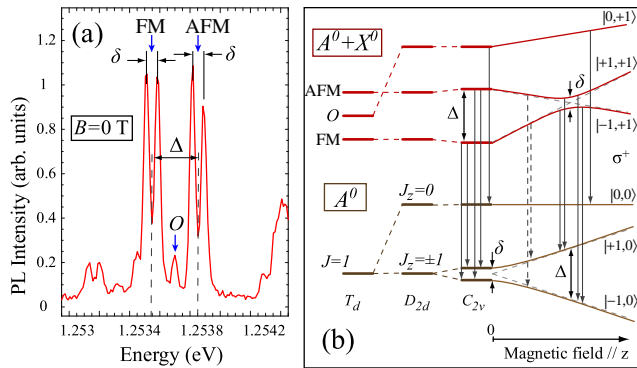


FIG. 1 (color online). (a) Micro-PL spectrum of an individual InAs quantum dot doped with a single Mn atom in zero magnetic field at $T = 2$ K. These lines were identified as originating from a charged exciton X^- . (b) Schematic of the excitonic transitions from $A^0 + X^0$ (initial state) to A^0 (final state) taking into account the local potential anisotropy and a longitudinal magnetic field. For simplicity only the bright states corresponding to σ^+ polarized transitions are shown. The same diagram holds for $A^0 + X^-$ (see text) by replacing the above labels by $|J_z, +3/2\rangle$ ($|J_z, +1/2\rangle$) in the initial (final) states, respectively.

case of exchange interaction between A^0 and X^0 , these levels are split into three doubly degenerate levels which read $|\pm 1, \pm 1\rangle$, $|0, \pm 1\rangle$, $|\mp 1, \pm 1\rangle$ corresponding to a FM, “orthogonal” (O), and AFM spin configuration, respectively. If the final A^0 states were perfectly degenerate, as predicted for the acceptor level in bulk GaAs, then we should observe in the PL spectrum three lines equally spaced and of identical intensity, similar to the six lines observed in CdTe QDs doped with a single Mn atom [12]. Actually, due to its hole component, the A^0 state is sensitive to local variations of composition and strain over a typical distance of 1 nm from the impurity center [16,19,20]. In self-assembled InAs QDs which resemble a flat lens of ~ 4 nm height, the most important perturbation of the bulk potential occurs along the growth direction z . Such a perturbation of D_{2d} symmetry shifts the $J_z = 0$ level to higher energy with respect to the $J_z = \pm 1$ states. In addition the potential experienced by the impurity has some in-plane anisotropy (with C_{2v} symmetry or lower), then the $J_z = \pm 1$ are further split by an energy δ . Such an effect is expected because the Mn impurity is very likely not in the center of the QD. Note that this anisotropy acts perturbatively as an off-diagonal term for the $A^0 + X^0$ levels which are already split by Δ . Following this scheme, the optical transitions from the FM and AFM levels appear as doublets due to the *final state* splitting, whereas the O level may recombine only to the $J_z = 0$ state because of orthogonality of its A^0 component ($J_z = 0$) with the $J_z = \pm 1$ states. The shift of the O level does not reflect in the transition energy, since it appears in both the initial and final states; however, it explains the weaker intensity observed experimentally for the O line because of A^0 thermalization in the $J_z = \pm 1$ levels.

The main support of this interpretation comes from the evolution in a longitudinal magnetic field. Thanks to the Zeeman effect it is possible to restore the A^0 eigenstates to $J_z = \pm 1$. The FM and AFM doublets should transform to single lines for a field $B_z > \delta/2g_1\mu_B$ where g_1 is the A^0 g factor in the $J = 1$ spin configuration and μ_B is the Bohr magneton. Taking the value $g_1 = 2.77$ found for GaAs:Mn [16], the typical magnetic field required amounts to only 230 mT for the QD shown in Fig. 1. In parallel, the magnetic field splits the FM and AFM levels by the sum of Zeeman effects for A^0 and X^0 . Therefore, the Zeeman splitting of A^0 does not reflect straightforwardly in the PL spectra apart from the “forbidden” transitions involving a spin flip of A^0 and represented by dashed arrows in Fig. 1(b). When the magnetic field reaches the value $\Delta/2g_1\mu_B$ (~ 1 T in our case) the $|+1, +1\rangle$ and $|-1, +1\rangle$ states are now brought into coincidence. Since they are formed with the same exciton spin, the anisotropic interaction between the $J_z = \pm 1$ levels splits the $A^0 + X^0$ levels by the same energy splitting δ as in zero field. For this very specific field the PL spectrum should thus be quite similar to the spectrum in zero field as illustrated in Fig. 1(b), with the splitting Δ (δ) in the final (initial) states.

To study the magnetic field dependence of the X^0 -to- A^0 coupling, we recorded a series of 121 μ -PL spectra over a 10 meV-energy range, by varying the magnetic field from -3 T to $+3$ T with a step of 50 mT. The detection was set σ^+ to help identify the different levels and their interactions. The μ -PL intensity was plotted on a color scale against magnetic field and energy detection, using an interpolating function for graphical rendering. To focus on the spin-dependent interactions we subtracted the diamagnetic shift $\propto B_z^2$. Figure 2 displays three spectral regions of this contour plot, showing clearly correlated spectral lines that could be identified (after a careful analysis) as the three excitonic features X^0 , $2X^0$, and X^- originating all from the same individual QD. Remarkably, the $2X^0$ and X^- set of lines is separated from X^0 by roughly the same binding energies as in undoped InAs QDs emitting at ~ 1.25 eV [21]. Note Fig. 1(a) is the cross section at $B = 0$ T of the X^- contour plot.

The main feature common to the plots of Fig. 2 is a very peculiar pattern resulting from the evolution of the zero-field doublets to another pair of doublets at $B \approx 0.75$ T. The resulting crossing lines correspond to the forbidden transitions involving A^0 spin flip from $J_z = \pm 1$ to $J_z = \mp 1$, respectively. Obviously these transitions are not strictly forbidden because of the anisotropic coupling either in the final state (at $B = 0$) or in the initial state (at $B \approx 0.75$ T). Focusing on the X^- feature, we clearly observe a strong evolution of the intensity ratio between the FM and AFM lines due to the A^0 thermalization on one of the $J_z = \pm 1$ levels depending on the field direction [22]. For $B_z > 0$, the $|+1, +1\rangle$ ($|-1, +1\rangle$) population should decrease (increase). Actually, it is this simple feature which allowed us to ascribe confidently the low energy doublet FM to the ferromagnetic $A^0 + X^0$ configuration. We note that such an effective ferromagnetic coupling was already reported by Szczytko *et al.* [23] in very dilute $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x < 0.001$).

In each case shown in Fig. 2, an exact replica of the main pattern is found at lower energy. We ascribe them to temporal electrostatic fluctuations of the QD environment which rigidly shift all the excitonic lines, e.g., due to charge trapping and detrapping in the QD vicinity. Since these replica were not found for other Mn-doped QDs that we have examined (and showing also the same crosslike patterns), we conclude that they are not related to the intrinsic signature of a Mn impurity. We chose to show this particular dot because three excitonic complexes were simultaneously visible with a high signal-to-noise ratio.

Another striking feature is the symmetry between X^0 and $2X^0$. It results from the polarization correlation in the biexciton cascade imposed by the Pauli principle. As we detect only σ^+ photons the measured transitions from $2X^0$ lead to the σ^- polarized X^0 , which obviously has the same field dependence as the σ^+ polarized X^0 but for $B_z \rightarrow -B_z$. This observation strongly supports the line identification and actually indicates that the biexciton (with both holes and electrons in singlet spin configuration) has no

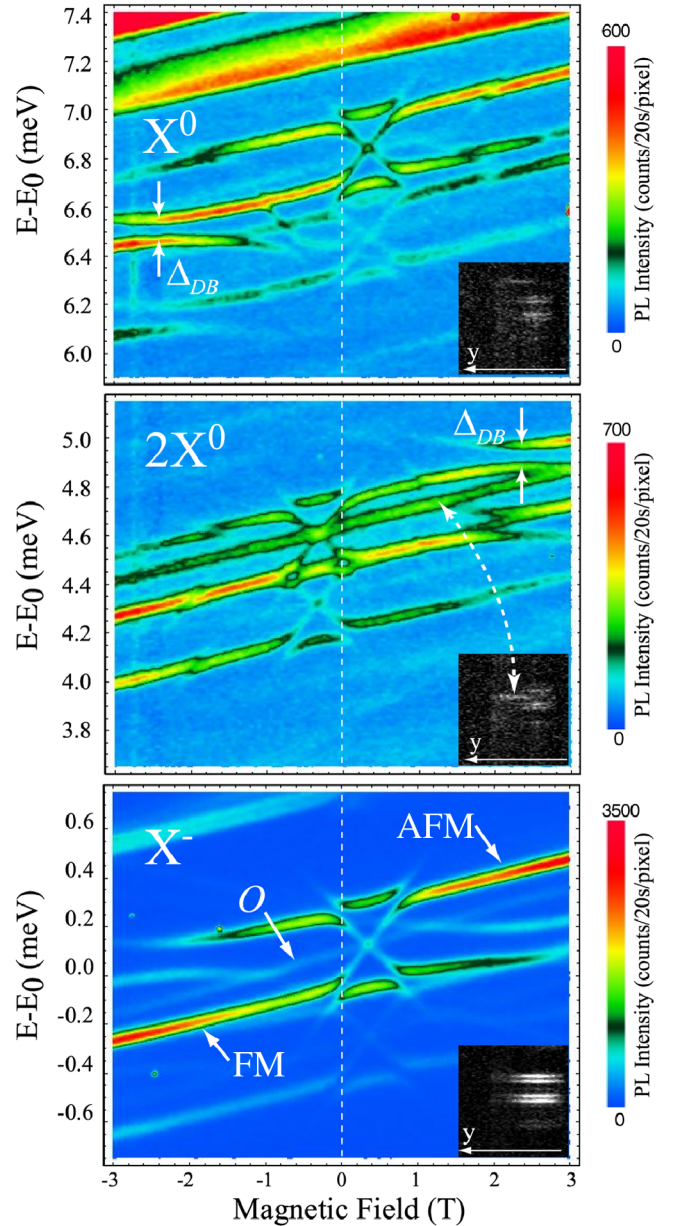


FIG. 2 (color online). Contour plot of μ -PL intensity from a single InAs QD doped with a single Mn impurity against longitudinal magnetic field and detection energy $E - E_0$ ($E_0 = 1.2536$ eV). The three energy windows correspond to the X^0 , $2X^0$, and X^- states observed in the same μ -PL spectra. Insets: CCD images ($100 \text{ pixels} \times \sim 150 \text{ pixels}$) at $B_z = 0$ T showing the spatial correlations of the lines along the vertical axis y of the setup. An extra line coming from another QD (dashed arrow) is superposed on the $2X^0$ feature.

spin interaction with the Mn impurity. Note that the very same symmetry has been observed in Mn-doped CdTe QDs [13].

Finally, the position of the crosslike pattern for the X^- case is very instructive. It reveals that one of the electron- A^0 or hole- A^0 exchange integrals must be vanishingly small with respect to the other. If not, the mixing at $B_z = 0$ between the $J_z = \pm 1$ states would be reduced both

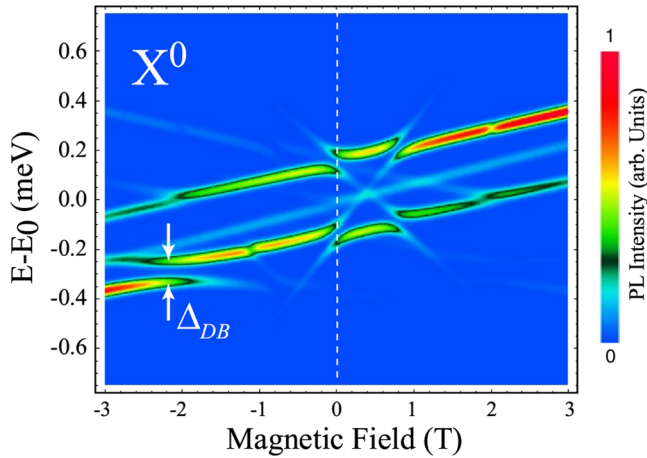


FIG. 3 (color online). Theoretical contour plot of X^0 PL intensity from a single InAs QD doped with a single Mn impurity against longitudinal magnetic field and energy.

in the initial state (due to hole- A^0 exchange) and final state (due to electron- A^0 exchange). There would be no splitting and the crosslike pattern would be shifted to a different field. Since it appears at the same positive field as for X^0 , the X^- transitions must be described by the diagram of Fig. 1(b), yet with $e-A^0$ as the final state. We can therefore conclude that the electron- A^0 coupling is negligible as compared to δ (actually below $20 \mu\text{eV}$ from a precise comparison of the spectra at $B_z = 0$).

To support the above discussion, we have modeled the spin interactions with the Mn impurity for the three excitonic configurations. To reproduce all details of our experimental results, it appeared necessary to include not only the $J = 1$ states of A^0 but also the $J = 2$ states. Our model includes the Zeeman Hamiltonian for a single particle (Mn, bound hole h_1 , QD S -shell hole h_2 , and electron e), strain Hamiltonian for h_1 [20], valence band mixing between light and heavy components for h_2 [24], and exchange interaction within each pair of particles. A detailed discussion of this model will be published elsewhere. We present in Fig. 3 the contour plot of theoretical PL spectra corresponding to the X^0 - A^0 configuration. By adjusting strain and exchange parameters, our model reproduces remarkably well the crosslike pattern, the effect of Mn thermalization ($T_{\text{Mn}} = 10 \text{ K}$), as well as the anticrossing Δ_{DB} observed at -2 T . The latter results from a coupling between the bright FM exciton $|+1, +1\rangle$ and the dark AFM exciton $|+1, -2\rangle$ when they are brought into coincidence by the field. Our model reveals that this is a resonant third order coupling involving the h_2 valence band mixing, a shear strain ϵ_{xz} (which also contributes to δ), and the effective h_2 - A^0 exchange constant Δ_{12} between the A^0 spin subspaces $J = 1$ and $J = 2$. It reads $\Delta_{12} = \epsilon_{h_2\text{-Mn}} - \epsilon_{h_1\text{-}h_2}$ where $\epsilon_{\alpha\text{-}\beta}$ is the exchange integral between the spins J_α and J_β . To reproduce our experimental results we found that the FM-AFM splitting Δ is dominated by this exchange term Δ_{12} while the exchange term

$\Delta_{11} = (7\epsilon_{h_2\text{-Mn}} - 3\epsilon_{h_1\text{-}h_2})/4$ within the $J = 1$ subspace contributes less than 10% of Δ .

In conclusion, the successful μ -PL investigation in a longitudinal magnetic field of a single Mn-doped InAs quantum dot reveals remarkable features bringing new insights into the spin interactions between carriers and a Mn impurity in a III-V matrix. The antiferromagnetic coupling between the hole bound to the magnetic impurity and the $3d^5$ Mn electrons is confirmed. In contrast, the effective coupling of the Mn impurity as a whole ($A^- + h$) with a hole confined in an InAs QD is proven to be ferromagnetic, while it essentially vanishes for a confined electron. The influence of the strain field on the Mn acceptor level is clearly evidenced, and gives rise to a very specific spectral signature of the Mn doping. Our results reveal that the Mn spin in A^0 configuration represents a two-level system well separated from higher energy levels which opens new outlooks for spin-based quantum information processing, e.g., by exploiting the exchange interaction with optically polarized carriers.

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