Geometrical Effects on the Optical Properties of Quantum Dots Doped with a Single Magnetic Atom

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The emission spectra of individual self-assembled quantum dots containing a single magnetic Mn atom differ strongly from dot to dot. The differences are explained by the influence of the system geometry, specifically the in-plane asymmetry of the quantum dot and the position of the Mn atom. Depending on both these parameters, one has different characteristic emission features which either reveal or hide the spin state of the magnetic atom. The observed behavior in both zero field and under magnetic field can be explained quantitatively by the interplay between the exciton-manganese exchange interaction (dependent on the Mn position) and the anisotropic part of the electron-hole exchange interaction (related to the asymmetry of the quantum dot).

Precise control of electronic spins in semiconductors should lead to the development of novel electronic systems based on the carriers' spin degree of freedom. These so-called spintronics devices, combining manipulation of charges and manipulation of spins, could complement or replace existing electronic systems, yielding new performances [1,2]. Magnetic semiconductor quantum dots (QDs), where excitons (electron-hole pairs) can interact strongly with the magnetic atoms, hold particular promise as building blocks for such spin-based systems. However, the geometric factors that become more and more important with decreasing QD size (because of the quantum confinement) need to be considered with great care [3]. For instance, any in-plane asymmetry can introduce very strong effects in the case of small dots (energy shift of the quantum levels, induced linear polarization) as revealed by single dot optical spectroscopy [4,5]. Thus it is crucial, with nanometric scale magnetic objects, to understand and to control all the geometric parameters which characterize the system.

In the case of a quantum dot incorporating a single magnetic atom (spin S) and a single confined exciton, the exchange interaction between the exciton and the magnetic atom acts as an effective magnetic field, so that the atom's spin levels are split even in the absence of any applied magnetic field [6]. A set of $2S + 1$ discrete emission lines can be resolved, providing a direct view of the atom's spin state at the instant when the exciton annihilates. However, there has been no experimental study of how a nonideal dot geometry, especially departures from circular or square symmetry for self-assembled QDs grown by molecular beam epitaxy (MBE), affects optical monitoring of the magnetic spin state.

This Letter concerns quantum dots containing a single manganese magnetic atom. We will show that the electron-hole-Mn system is very sensitive to the geometry, specifically the asymmetry of the QD and the position of the Mn atom in the dot. We report experimental results showing

the three different types of spectra possible. Control of both the exciton-manganese (X-Mn) exchange interaction (determined by the position of the Mn) and the anisotropic electron-hole (e-h) exchange interaction (related to the shape of the dot) appears as a key condition for detection and manipulation of the spin state of the isolated magnetic atom. A strong interaction between the exciton and the Mn splits the six Mn spin components, but a strong anisotropy of the dot perturbs the spectrum pattern and can hide the information on the Mn spin state.

Single Mn atoms are introduced into CdTe/ZnTe QDs during their growth by MBE, adjusting the density of Mn atoms to be roughly equal to the density of dots [7]. The samples provide symmetric (disclike) dots and asymmetric (ellipsoidal) dots, containing Mn atoms at various positions. The QD emission (at $\simeq 2$ eV) is studied in magnetic fields ($B = 0$ to 11 T) by optical microspectroscopy in Faraday configuration under nonresonant laser excitation.

Figure 1 shows the three types of emission spectra obtained at 5 K, under low excitation density, for single QDs containing a single Mn. In the first example (QD1), a structure composed of six main lines dominates the emission spectrum at zero magnetic field. Such a spectrum is a fingerprint of a confined exciton interacting with a single Mn atom [6]. These lines correspond to the radiative ("bright") exciton states $J_z = \pm 1$ coupled to the six spin components of the Mn atom ($S = 5/2$). Analysis of the line intensities gives the occupation probability of the six Mn spin states [6]. The three low intensity lines on the low energy side of the structure [Fig. 1(a)] can be attributed to the contribution of exciton dark states [6]. We will see that a fine structure with well separated lines requires not only that the Mn atom interact strongly with the exciton in the dot, but also that the dot must retain high symmetry.

By contrast, the emission of QD2 consists of two broad peaks with width about 200 μeV, separated by an energy gap of about 300 μeV. A similar gap is seen clearly in the third example (QD3), for which six lines are observed, but
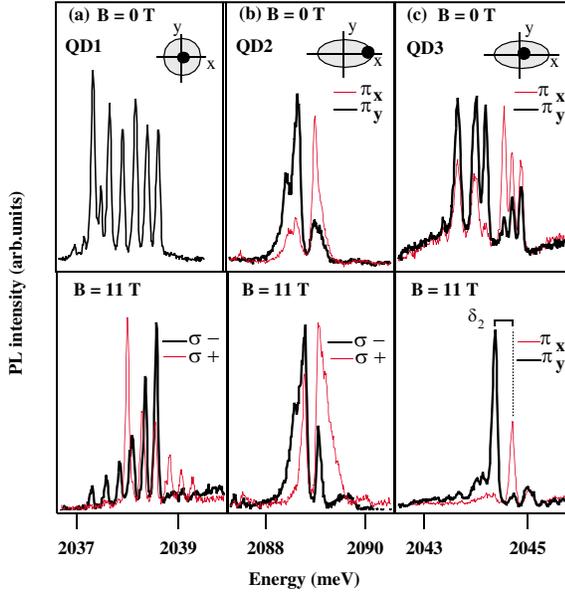
FIG. 1 (color online).   Low temperature ($T = 5$ K) photoluminescence (PL) spectra of three different Mn-doped CdTe/ZnTe QDs at $B = 0$ T and $B = 11$ T. $\sigma_{\pm}$ are circular polarizations and $\pi_{x,y}$ are two orthogonal linear polarizations. (a) Exciton strongly coupled with a Mn atom, in a symmetric dot. (b) Exciton less strongly coupled with a Mn atom, in an asymmetric dot. (c) Exciton strongly coupled with a Mn atom, in an asymmetric dot.

with two sets of three lines separated by the central gap. An additional essential property is that the emission lines are linearly polarized along two orthogonal directions for QD2 and QD3, whereas for QD1 the emission is unpolarized.

Such large differences in the zero field emission spectra can be attributed to competition between the X-Mn interaction and the anisotropic e-h exchange interaction arising in asymmetric QDs. We recall that, for nonmagnetic QDs, the e-h exchange interaction in an anisotropic potential mixes the bright exciton states $J_z = \pm 1$. The emission of the QD is then linearly polarized along two orthogonal directions and split by the anisotropic exchange energy δ_2 [4,8], originating from the long range (nonanalytic) e-h exchange interaction H_{e-h}^{aniso} [9].

In symmetric Mn-doped QDs, the X-Mn exchange interaction lifts the degeneracy of the bright exciton states, the splitting being proportional to the Mn spin projection S_z [6]. Such systems can be described by an effective Hamiltonian $H = I_e s_e \cdot S + I_h j_h \cdot S + H_{e-h}^{\mathrm{iso}}$ operating in the basis of the heavy-hole exciton states and Mn spin states. Here, I_e (I_h) is the electron (hole)-Mn exchange integral and s_e, j_h, and S are, respectively, the electron, heavy-hole, and Mn spins. H_{e-h}^{iso} is the isotropic part of the e-h exchange interaction. In zero magnetic field, there are six doubly degenerate radiative energy levels formed by associating the six Mn spin projections with the two bright exciton states $J_z = \pm 1$ (the corresponding transitions lie on the dotted cross in Fig. 2). They are separated by equal energy intervals $\delta_{\mathrm{Mn}} = \frac{1}{2}(I_e - 3I_h)$.

We now consider how the simultaneous presence of H_{e-h}^{aniso} and the X-Mn exchange interaction affects the zero field spectrum. Diagonalizing the augmented Hamiltonian $H + H_{e-h}^{\mathrm{aniso}}$ shows that the e-h exchange interaction splits the six-line structure into two subsets of three lines. Figure 2 represents the bright state transitions ($J_z = \pm 1$) associated with the six manganese spin projections S_z. The anisotropic e-h exchange term δ_2 mixes the bright exciton states associated with the same Mn spin projection, inducing an extra splitting between them. The energy splitting of the bright excitons for a given value of S_z is given by

$$\Delta E(S_z) = \sqrt{\delta_2{}^2 + (2|S_z|\delta_{Mn})^2}, \qquad (1)$$

where $2|S_z|\delta_{\mathrm{Mn}}$ is the splitting induced by the Mn only. The mixing induced by δ_2 is thus strongest for the central pair of states, associated with the $S_z = \pm 1/2$ Mn spin projections. Equation (1) for $\Delta E(S_z)$ shows that the anisotropy of the dot creates a gap in the center of the emission structure; see Fig. 2. This explains the line patterns observed for the three types of QD spectra presented above.

The width of the central gap ($\sqrt{\delta_2{}^2 + \delta_{\mathrm{Mn}}{}^2}$) and the width of the whole six-line spectrum structure ($\sqrt{\delta_2^2 + (5\delta_{\mathrm{Mn}})^2}$) yield the values of δ_2 and δ_{Mn} for the three dots of Fig. 1. The ratio $\delta_2/\delta_{\mathrm{Mn}}$ determines the spectrum type. For QD1, the ratio $\delta_2/\delta_{\mathrm{Mn}}$ is found to be <0.2, with $\delta_{\mathrm{Mn}} = 250$ μeV: the X-Mn interaction dominates the emission structure and the Mn spin states are directly resolved in the optical spectrum. By contrast, $\delta_2/\delta_{\mathrm{Mn}} = 2.3$ for QD2 ($\delta_{\mathrm{Mn}} = 120$ μeV), so the anisotropy splitting predominates: we observe only two broad peaks separated by a central gap and can no longer resolve the Mn spin states. A reduction in δ_{Mn} of only a factor of 2 has completely changed the type of spectrum. QD3 demonstrates the intermediate case ($\delta_2/\delta_{\mathrm{Mn}} = 1.3$, with $\delta_{\mathrm{Mn}} = 230$ μeV) where the combined effect of the e-h and X-Mn exchange interactions is seen very clearly: despite the importance of anisotropy, the Mn spin states are still resolved as two subsets of three lines separated by the central gap.
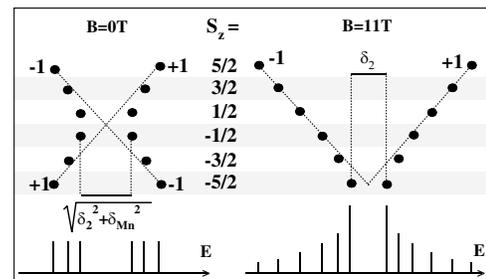

FIG. 2.   Bright state transitions in an asymmetric Mn-doped QD at $B = 0$ T and 11 T. The e-h exchange interaction induces anticrossings (energy δ_2) of the ± 1 excitons associated with $S_z = -1/2, -3/2, -5/2$ for successive values of B; the $S_z = -5/2$ anticrossing is shown to the right.

The parameter δ_{Mn} is determined [10,11] by the values of $I_e = \alpha|\phi_e(R_{Mn})|^2$ and $I_h = \beta/3|\phi_h(R_{Mn})|^2$. Here ϕ_e (ϕ_h) is the electron (hole) envelope function, which falls off with R_{Mn}, the distance of the Mn atom from the QD center; α (β) are the Mn-$e(h)$ exchange constants [12]. Clearly, for QD2, the Mn atom is farther from the dot center than for QD1 and QD3.

The theory also explains the linear polarization that we observe in zero magnetic field. When anisotropic electron-hole exchange interaction is included, the eigenstates of the X-Mn system are of the form [5,8]:

$$|+\rangle|S_z\rangle = (\cos\theta|+1\rangle + \sin\theta|-1\rangle)|S_z\rangle,$$
$$|-\rangle|S_z\rangle = (\cos\theta|-1\rangle - \sin\theta|+1\rangle)|S_z\rangle, \quad (2)$$

where $\tan 2\theta = \delta_2/(2|S_z|\delta_{Mn})$. The mixing of the bright states associated with a Mn spin state S_z is controlled by the ratio of δ_2 to the Mn induced splitting $2|S_z|\delta_{Mn}$. The emission lines have partial linear polarization along two orthogonal directions corresponding to the principal axes of the anisotropic potential. Figure 3 compares measured and theoretical degree of polarization for QD3. The data are in qualitative agreement with the theoretical curve. In particular, central lines $E3$ and $E4$, associated with $S_z = \pm 1/2$, are almost completely polarized. The expected decrease with increase of $\Delta E(S_z)$ is reproduced qualitatively especially for the three upper energy lines $E4$, $E5$, and $E6$. For the lower energy lines, the degree of polarization could be influenced by the nonradiative states ($J_z = \pm 2$) which lie in their energy range.
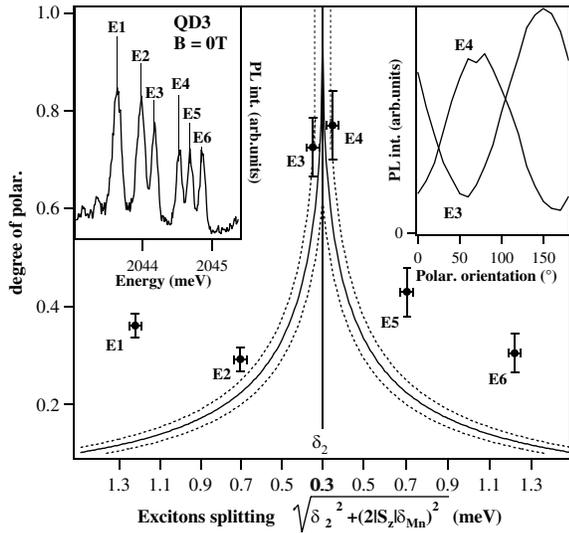
Our interpretations of the above spectra are confirmed by magneto-optical measurements (Figs. 1, 4, and 5). For QD3 [Fig. 4(a)] and QD1 [Fig. 5(a)], the typical Zeeman splitting of the six lines is clearly observed in the data at all fields, with a strong intensity gradient at the highest fields (see Fig. 1) resulting from a rather strong Mn spin polarization. For the clearly anisotropic dots [QD3 and QD2, Fig. 5(b)], the central gap in the emission structure is maintained in both circular polarizations, with a small quadratic diamagnetic energy shift. This behavior is explained as follow. The dot anisotropy leads to successive anticrossings of the ± 1 exciton states associated with given Mn spin projections ($-1/2$, $-3/2$, and $-5/2$) as a function of magnetic field: As B increases, transitions associated with the $J_z = +1$ exciton shift up in energy, whereas the $J_z = -1$ transitions shift down (see Fig. 2). The anisotropic part of the electron-hole exchange interaction mixes successively the $J_z = \pm 1$ exciton states associated with $S_z = -1/2$, then with $S_z = -3/2$, and finally with $S_z = -5/2$ at successively higher B. For QD3, these anticrossings are observed successively at 2.5, 7, and 11 T.

To understand fully the rich magnetic behavior of dots like QD3, we calculated the optical transitions under magnetic field by diagonalizing the complete Hamiltonian of the electron-heavy-hole-Mn system (including the ex-

FIG. 3. Measured degree of linear polarization of emission lines $E1$–$E6$ for QD3 in zero field, as a function of the splitting between the $|J_z = \pm 1, S_z\rangle$ states, compared to theoretical behavior (solid curves; dotted curves show the uncertainty range corresponding to the imprecision in δ_2). The left inset labels the emission lines. The right inset shows the PL intensity of the lines $E3$ and $E4$ ($S_z = \pm 1/2$), as a function of the linear polarizer orientation.
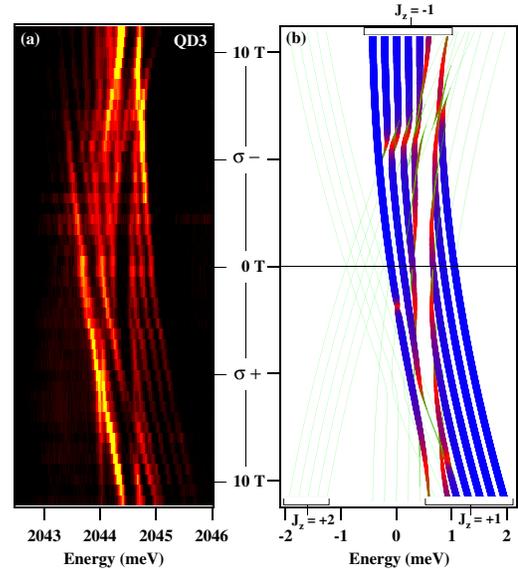

FIG. 4 (color online). (a) Intensity map of magnetic field dependence of the emission spectrum of asymmetric Mn-doped dot QD3, for circular polarization $\sigma+$ and $\sigma-$. (b) Optical transitions obtained from the diagonalization of the spin + Zeeman + diamagnetism Hamiltonian in the subspace of the 24 heavy-hole exciton and Mn spin components. Line thickness and color scale for $\sigma+$, $\sigma-$ are proportional to absolute value of the projection of the exciton state on the $J_z = +1$, -1 exciton, respectively (green or light gray scale is low intensity, and blue or dark gray scale is high intensity). The two transitions which are forbidden at all magnetic fields ($|J_z = \pm 2, S_z = \mp 5/2\rangle$) are not plotted.

change, Zeeman and diamagnetism Hamiltonians). Calculated transitions are presented in Fig. 4(b). The fitted Landé factors of the electron ($g_e = -1.1$), the hole ($g_h = 0.3$) and the Mn atom ($g_{Mn} = 2.0$), the splitting between $J_z = \pm 1$ and $J_z = \pm 2$ excitons ($= 1$ meV), and the diamagnetic factor ($\gamma = 2.45 \ \mu\text{eV} \cdot \text{T}^{-1}$) agree well with previous work [5,6,12]. Parameters δ_2 and δ_{Mn} were adjusted to fit the zero field data, as explained earlier.

Comparison between calculation and data explains most of the details of the magneto-optic properties of QD3. In particular, around 7 T, the central gap is perturbed in both circular polarizations. In $\sigma-$, this is due to anticrossings induced by the mixing of $|s_{ez} = 1/2, j_{hz} = -3/2, S_z\rangle$ states and $|-1/2, -3/2, S_z + 1\rangle$ states by the *electron*-Mn exchange, [6], i.e., corresponding to simultaneous spin-flips of electron and manganese spins. In $\sigma+$ polarization, Fig. 4(b) shows that the line of second lowest energy crosses the central gap as an essentially nonradiative transition. This implies a mixing of $|-1/2, 3/2, -3/2\rangle$ and $|-1/2, -3/2, -1/2\rangle$. This is a second order mixing involving both mixing of $|-1/2, -3/2, -1/2\rangle$ and $|1/2, -3/2, -3/2\rangle$ by the *e*-Mn exchange and mixing of $|-1/2, 3/2, -3/2\rangle$ and $|1/2, -3/2, -3/2\rangle$ by the anisotropic *e-h* exchange; that is, the *e*-Mn exchange induces a mixing of states mediated by the anisotropy-induced coupling.

We now consider the field dependence of the two extreme cases illustrated by QD1 and QD2. For QD2 [Fig. 5(b)], where $\delta_2/\delta_{Mn} = 2.3$, the field dependence is mainly the quadratic variation of the central gap. At $B = 11$ T, the Zeeman splitting has nevertheless separated the ± 1 excitons and the circular polarization is almost completely restored [Fig. 1(b)]. The perturbation of the central gap around 4 T in $\sigma-$ polarization can be attributed, as for QD3, to the mediating electron-hole exchange.

QD1 presents weak anticrossings [see insets in Fig. 5(a)] that are not explained by the simple model of a Mn-doped symmetric QD. By comparing with calculations, we can attribute these anticrossings to a slight anisotropy, too small to be revealed by the presence of a clear central gap at zero field: the perturbation occurring from 5 to 9 T in $\sigma+$ polarization corresponds to a mixing between bright states associated with Mn spin projection $-1/2$, and represents a residue of the central gap discussed extensively above. The other anticrossings involve bright ($J_z = \pm 1$) and dark ($J_z = \pm 2$) states and are due to second order electron-Mn exchange interaction mediated by the anisotropic *e-h* exchange interaction, as seen more clearly in the strongly anisotropic QDs.

In summary, we demonstrate that the position of a single Mn atom in a QD is not the only parameter that has to be controlled in order to resolve the Mn spin states. Another geometric parameter must be considered: the asymmetry of the dot. The interplay between these two parameters has important consequences for the QD optical properties. The Mn-exciton exchange interaction tends to separate the bright exciton states, whereas the anisotropic part of the
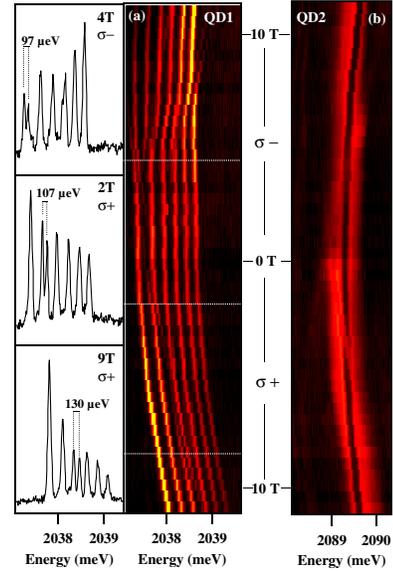

FIG. 5 (color online). Magnetic field dependence of the emission of QD1 and QD2. (a) Exciton strongly coupled with a single manganese atom, in a quasisymmetric dot. Anticrossings discussed in the text are illustrated by the spectra in the left insets. (b) Exciton less strongly coupled with a manganese atom, in a symmetric dot.

electron-hole exchange interaction tends to couple them and to hide the Mn spin splitting. The wealth of data obtained gives a unified picture of the effects of dot asymmetry on the fine structure and polarization properties of optical transitions in single Mn-doped QDs. This allows us to determine the conditions required to tune the magnetic QD states in order to control and manipulate individual localized spins by single carriers.

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[1] B. E. Kane *et al.*, Nature (London) **393**, 133 (1998).
[2] D. Loss and D. P. DiVincenzo, Phys. Rev. A **57**, 120 (1998).
[3] M. Bayer *et al.*, Phys. Rev. Lett. **82**, 1748 (1999).
[4] V. D. Kulakovskii *et al.*, Phys. Rev. Lett. **82**, 1780 (1999).
[5] L. Besombes, K. Kheng, and D. Martrou, Phys. Rev. Lett. **85**, 425 (2000); L. Besombes *et al.*, J. Cryst. Growth **214**, 742 (2000).
[6] L. Besombes *et al.*, Phys. Rev. Lett. **93**, 207403 (2004).
[7] F. Tinjod *et al.*, Appl. Phys. Lett. **82**, 4340 (2003).
[8] E. L. Ivchenko, Phys. Status Solidi (a) **164**, 487 (1997).
[9] G. E. Pikus, Sov. Phys. JETP **33**, 108 (1971).
[10] A. K. Bhattacharjee and J. Pérez-Conde, Phys. Rev. B **68**, 045303 (2003).
[11] F. V. Kyrychenko and J. Kossut, Phys. Rev. B **70**, 205317 (2004).
[12] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).