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Carrier-induced spin splitting of an individual magnetic atom embedded in a quantum dot

L. Besombes,* Y. Leger, L. Maingault, D. Ferrand, and H. Mariette
CEA-CNRS Group Nanophysique et Semiconducteurs, Laboratoire de Spectrométrie Physique, CNRS and Université J. Fourier-Grenoble I, Boîte Pôstale 87, F-38402 St Martin d'Heres, France

J. Cibert
Laboratoire Louis Néel, CNRS, Boîte Postale 166X, F-38042 Grenoble, France
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The influence of the number of confined carriers on the spin splitting of a single magnetic ion (Mn^{2+}) embedded in a semiconductor quantum dot is evidenced. Investigating both the biexciton and the exciton transitions in the same Mn-doped quantum dot, we analyze the impact of the Mn-exciton exchange interaction on the fine structure of the quantum dot emission. A single electron-hole pair is enough to induce a spontaneous splitting of the exciton-Mn system. The injection of a second electron-hole pair cancels the exchange interaction with the Mn ion and the Mn spin splitting is significantly reduced. A detailed analysis of the biexciton-Mn transitions reveals that the carriers' orbital wave functions are perturbed by the interaction with the magnetic ion.

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Several proposals for quantum information storage and processing using electron spins in quantum dots (QDs) have been put forward recently. Spin qubits are an attractive choice for the development of solid-state quantum information processing devices due to their long coherence time.[1,2] Developing such devices requires, however, the ability to detect and manipulate individual spins. Magnetic ion-doped QDs seem promising for the detection and manipulation of spins in the nanometer scale.[3] They have been proposed as single-spin filters or single-spin aligners for quantum computing applications.[4] QDs based on *II-VI* semiconductor compounds offer the unique possibility of incorporating magnetic ions (Mn^{2+}) isoelectronically into the crystal matrix.[5] This provides a way to study the interaction between a controlled number of injected carriers and the localized magnetic ions. In this paper, we analyze the influence of the number of confined carriers on the spin splitting of a single magnetic ion embedded in an individual QD. Investigating both the biexciton and the exciton transitions in the same Mn-doped QD, we analyze the impact of the Mn-exciton exchange interaction on the fine structure of the QD emission. A single electron-hole pair is enough to induce a spontaneous splitting of the exciton-Mn system and a slight polarization of the Mn spin distribution. The injection of a second electron-hole pair cancels the exchange interaction with the Mn ion and the Mn spin degeneracy is almost completely restored. The remaining splitting arises from a perturbation of the carriers orbital wave functions induced by the potential energy created by the localized magnetic ion.

We use magneto-optic microspectroscopy to analyze the optical properties of individual Mn-doped self-assembled CdTe/ZnTe QDs. Single Mn atoms are introduced in CdTe/ZnTe QDs (Ref. 6) by adjusting, during the growth process, the density of Mn atoms to be roughly equal to the density of QDs.[7] The photoluminescence (PL) of individual QDs is excited with the 488 nm line of an argon laser and collected through aluminium 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 Charge-coupled device (CCD).

In the following, we will first compare the fine structure of the exciton and biexciton in a single Mn-doped QD and then analyze in detail the influence of the Mn atom on the carriers orbital wave functions. Figure 1 shows the emission spectra of one of these Mn-doped QD for various excitation densities. At low excitation, a structure composed of six major lines, labeled *X*-Mn, dominates the spectra. An enlarged view of this emission structure is presented in the inset of Fig. 1. Following the work done in Ref. 8, the observation of this fine structure is attributed to a confined exciton interacting with a single Mn^{2+} ion. The six main lines corresponds to the bright exciton states ($J_z=\pm 1$) coupled with the six spin components of the Mn^{2+} ion ($S=5/2$). The energy splitting of these six lines depends on the Mn-carriers exchange interaction and is related to the position of the Mn atom into the QD. As the position of the Mn atom is not controlled, the observed splitting strongly differs from dot to dot. A maximum overall splitting of 1.3 meV has been measured in the QD presented in this paper. The three additional lines, observed at low-excitation intensity in the low-energy side of the emission structure, are due to the interaction of the dark exciton states ($J_z=\pm 2$) with the Mn^{2+} ion.[7] The electronic part of the exciton-Mn exchange interaction Hamiltonian[7,8] introduces a coupling between the bright and dark states allowing an optical observation of the dark states even at zero magnetic field. The PL contribution of the dark states is enhanced by the relaxation of the exciton-Mn system towards the low-energy levels. This relaxation is also responsible of the asymmetry in the emission intensity distribution of the bright states at low-excitation intensity.[7]

On increasing the excitation intensity, a new structure of six lines, labeled X_2-Mn appears 10.9 meV below the exciton lines. Its intensity increases quadratically at low excitation and its structure reproduces the spectral pattern of the exciton. Such intensity dependence has been observed in various QD systems and is regarded as a fingerprint of exciton and biexciton emission.[9,10] The energy difference between the

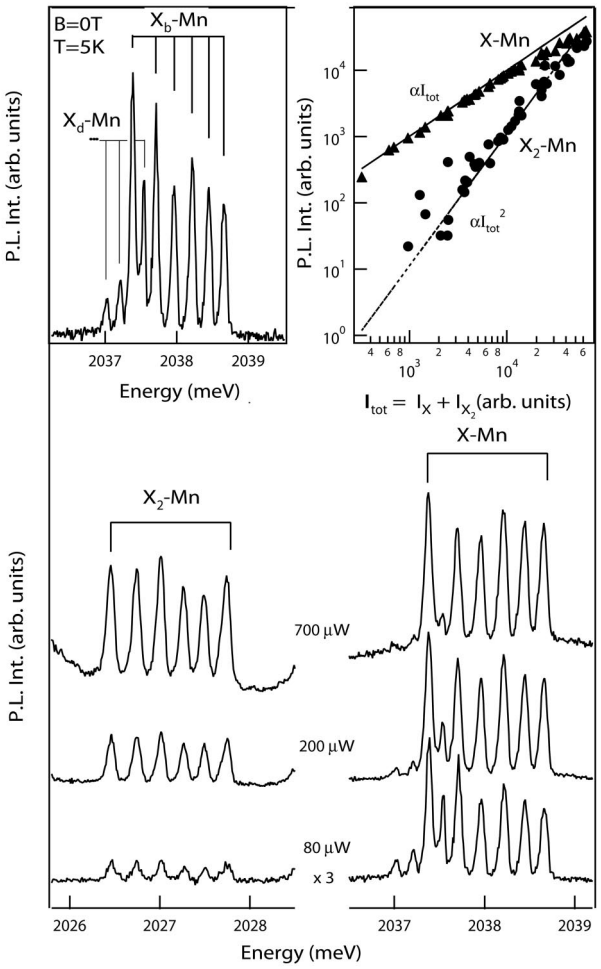

FIG. 1. PL spectra of a single Mn-doped QD for different excitation intensities. *X*-Mn denotes the exciton-Mn emission while X_2-Mn corresponds to the recombination of the two-exciton-Mn (biexciton) states. The insets give a detail of the *X*-Mn emission spectra at low-excitation density (X_b-Mn corresponds to the bright excitons and X_d-Mn corresponds to the dark excitons) and the evolution of the integrated intensities of *X*-Mn and X_2-Mn as a function of the total emission intensity.

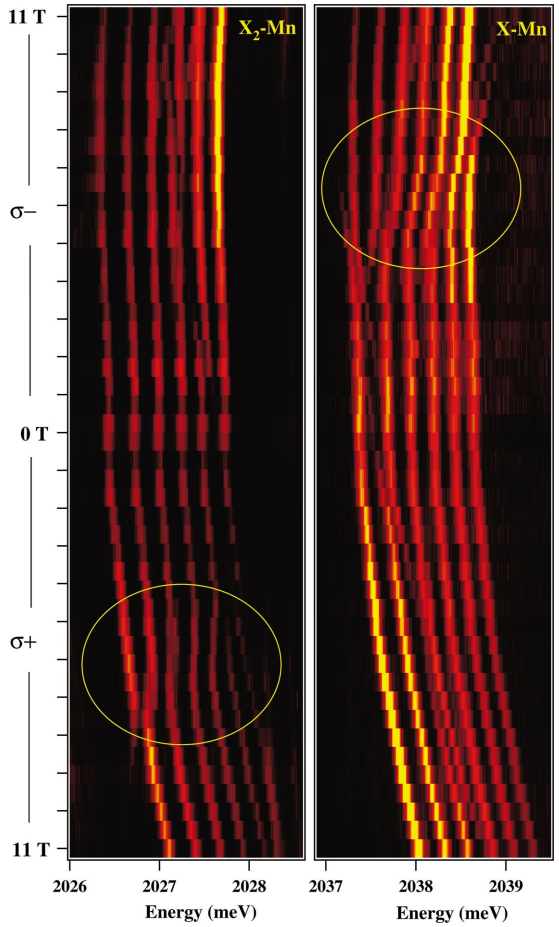

FIG. 2. (Color) Intensity contour plot of the magnetic field dependence of the excitonic and biexcitonic transitions of a single Mn-doped QD. The bright areas correspond to the high PL intensity. The anticrossings observed for the exciton are symmetrically reproduced on the biexciton transitions.

X-Mn and the X_2-Mn transitions (10.9 meV) corresponds to the typical binding energy of the biexciton measured in nonmagnetic CdTe/ZnTe QDs.[9] We have also noticed that, as the excitation intensity increases, the contribution of the transitions associated with the dark exciton states progressively vanishes. This evolution, already observed in nonmagnetic QDs,[9] is due to the longer lifetime of the dark exciton states. Because of this difference in lifetime, for a given nonresonant excitation intensity, the probability of creating a biexciton with two dark excitons is larger than with two bright excitons. The formation of the biexciton will then act as an efficient recombination channel for the dark exciton states and decrease their direct PL contribution.

Magneto-optic measurements confirm that the exciton and the biexciton transitions coming from the same Mn-doped QD are observed. The magnetic field dependence of the exciton-Mn and biexciton-Mn transitions energies are presented as a contour plot in Fig. 2. For *X*-Mn, six lines are observed in each circular polarization. Their energy follows the Zeeman and diamagnetic shift of the exciton in nonmagnetic QDs.[7] The excitonic transitions also present a rich fine structure mainly characterized by a series of five anticrossings observed in $\sigma-$ polarization around 7 T. These anticrossings come from the mixing of the bright and dark exciton states[7] induced by a simultaneous spin flip of the electron and Mn^{2+} ion. The fine structures of the exciton-Mn and the biexciton-Mn systems under magnetic field present a perfect mirror symmetry. The anticrossings observed on the high energy lines of *X*-Mn in $\sigma-$ polarization are symmetrically observed on the low-energy lines and in $\sigma+$ polarization for X_2-Mn. Some additional anticrossings, pointed by circles in Fig. 3(a), are also symmetrically observed for the exciton and the biexciton transitions. These tiny anticrossings arise from the electron-hole exchange interaction and a slight anisotropy of the QD.[11]

As it appears in the contour plot presented in Fig. 2, the relative intensities of the six emission lines observed in each circular polarization strongly depend 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 side of the $\sigma-$ emission and on the low-

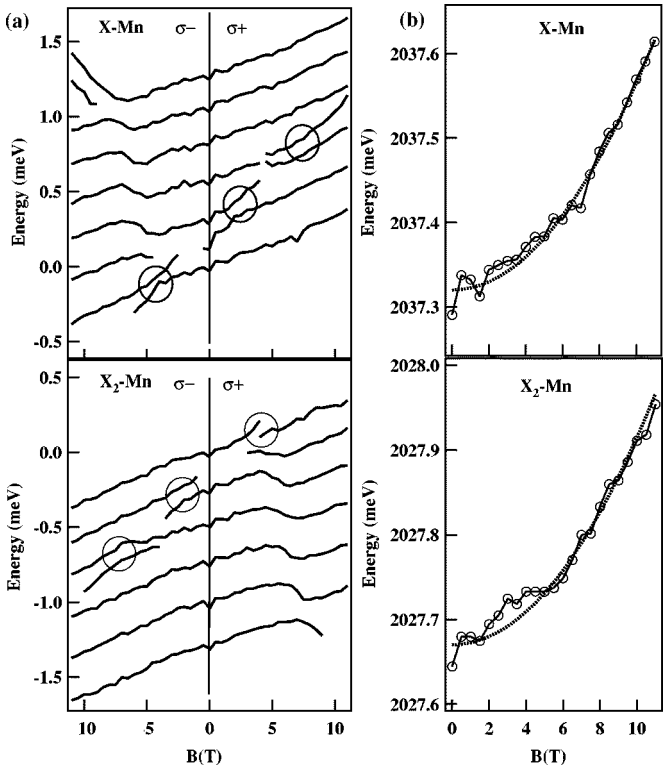

FIG. 3. (a) Exciton-Mn (X-Mn) and biexciton-Mn (X_2-Mn) transition energies as functions of a magnetic field after removing the diamagnetic shift. (b) The diamagnetic shift of the exciton-Mn and biexciton-Mn complexes. The dotted lines are parabolic fits with a diamagnetic shift coefficient $\Gamma_{X\text{-Mn}}=\Gamma_{X_2\text{-Mn}}=0.002\,45$ meV T^{-2}.

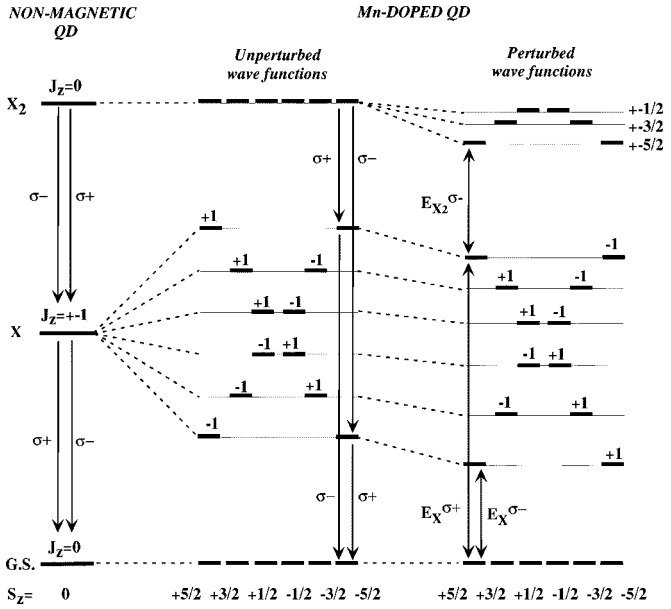

FIG. 4. Scheme of optical transitions from the exciton-Mn and biexciton-Mn states at zero magnetic field. The right-hand side scheme illustrates the effect of a perturbation of the carriers' orbital wave functions by the exchange coupling with the Mn^{2+} ion. Mn spin projections are indicated on the horizontal scale.

energy side of the σ+ emission at high magnetic field. The intensity distribution is similar for X-Mn and X_2-Mn.

In a QD, the biexciton ground state is a spin-singlet state ($J=0$) and cannot be split by the magnetic field or the spin interaction part of the carriers' Mn Hamiltonian.[12] In this model, the creation of two excitons in the same QD cancels all the exchange interaction terms with the Mn^{2+} ion. Thus, as illustrated in the center scheme of Fig. 4, the fine structure of the biexciton-Mn transitions is controlled by the final state of the recombination of the biexciton, i.e., the eigenstates of the exciton-Mn coupled system. The optical transitions directly reflect this mirror symmetry of the energy levels. Moreover, the intensity distribution of the X-Mn and X_2-Mn transitions are both controlled by the spin polarization of the Mn^{2+} ion. The spin of the Mn^{2+} ion is orientated by the applied magnetic field. At high field, when the biexciton recombines, the probability of leaving in the QD an exciton coupled with a Mn spin component $S_z=-5/2$ is enhanced. Therefore, in the two-photons cascade occurring during the recombination of a biexciton (Fig. 4, center scheme), the polarization of the Mn^{2+} spin will enhance the intensity of the high-energy biexcitonic transition in $\sigma-$ polarization and of the low-energy single-exciton transition in σ+ polarization. Symmetrically, the emission intensity is concentrated in the low-energy biexcitonic transition in σ+ polarization and in the high-energy single-exciton transition in $\sigma-$ polarization.

However, two important features of the spectra break this perfect symmetry of the exciton-Mn and biexciton-Mn transitions. First, as presented in Fig. 3(b), the diamagnetic shift of the center of the biexciton-Mn spectral lines is equal to the diamagnetic shift of the exciton-Mn system. The shift of the biexciton-Mn transitions is given by the difference of the biexciton-Mn diamagnetic shift in the initial states and of the exciton-Mn shift in the final states.[13] An identical shift for the exciton and biexciton shows that the biexciton-Mn diamagnetic shift is exactly twice the diamagnetic shift of the exciton-Mn system. As observed in nonmagnetic QDs, this result indicates that the excitonic wave functions are not significantly affected by the exciton-exciton interaction.[13,14]

Secondly, let us consider in details the exciton and the biexciton transitions at zero magnetic field [Fig. 5(a)]. If only the spin interaction part of the carrier-Mn Hamiltonian is considered, the six bright X-Mn transitions should be equally spaced in energy.[7] In fact, an irregular structure is observed and the energy spacing decreases from the low-energy side to the high-energy side of the emission pattern. In the framework of the effective spin Hamiltonian model,[7] the transitions energies of X_2-Mn are controlled by the energies of the X-Mn levels. This means that the structure of the X-Mn and X_2-Mn transitions should be perfectly symmetric. Surprisingly, the X-Mn and X_2-Mn transitions are found to be almost identical and not symmetric. This directly shows that the biexciton-Mn levels remain split and that their fine structures are not completely controlled by X-Mn in the final state of the biexciton-exciton transitions.

The irregular spacing observed for X-Mn likely comes from a correction to the exchange energy terms due to a perturbation of the electron and hole wave functions.[15] This perturbation is induced by the potential created by the Mn^{2+} ion and is equivalent to the orbital contraction of the carriers wave functions observed in the formation of a magnetic po-

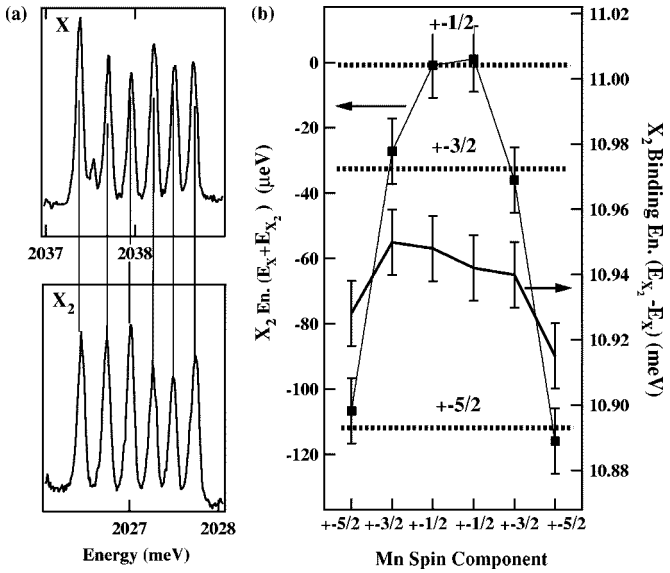

FIG. 5. (a) Detail of the exciton-Mn and biexciton-Mn transitions at zero magnetic field showing the irregular spacing of the transition energies. (b) Biexciton energies ($E_{X_2}+E_X$) and biexciton binding energies ($E_{X_2}-E_X$) deduced from the optical transitions presented in (a). The biexciton energies scale is translated by 4065.225 meV.

laron in higher dimensional systems.[16,17] In our case, the potential created by the magnetic ion is more or less attractive depending on the relative configuration of the Mn^{2+} and exciton spins. The resulting decrease of the X-Mn energy is expected to increase with the absolute value of the Mn spin component. An irregular structure is then obtained with a decrease of the splitting from the low-energy side to the high-energy side of the emission pattern (Fig. 4), as observed experimentally. This perturbation modifies the wave functions and will also affect the biexciton-Mn energies. Due to the presence of two electron-hole pairs, the perturbation of X_2-Mn is twice the perturbation of X-Mn, as already noticed for the diamagnetic shift. The biexciton-exciton transition will then reproduce exactly the perturbed structure of the exciton-Mn system, as observed in the PL spectra at zero field.

For a given Mn-spin component, the total energy of the biexciton-Mn complexes can be directly deduced from the X-Mn and X_2-Mn transitions energies at zero field. For instance, as illustrated in Fig. 4, in the case $S_z=+5/2$, this energy is given by $E_{X_2}^{\sigma-}+E_X^{\sigma+}$. The result obtained for all the different spin components are presented in Fig. 5(b). Three biexciton energy levels are obtained with an overall splitting of about 100 μeV. The energy of X_2-Mn depends on the absolute value of the Mn^{2+} spin. The most stable biexcitonic complex is associated with a Mn^{2+} spin projection $S_z=\pm 5/2$ corresponding to the largest exchange coupling with the exciton and consequently, the largest perturbation in the exciton wave functions. Despite this perturbation, the binding energy of the biexciton ($E_X^{\sigma-}-E_{X_2}^{\sigma-}$) is found to be almost constant. This binding energy comes from the balance of the attractive and repulsive Coulomb terms and is not significantly affected by the presence of the Mn^{2+} ion.

In summary, we have shown that the optical injection of a controlled number of carriers in an individual QD permits to control the spin splitting of a single magnetic ion. The exchange interaction with a single exciton acts as an effective local magnetic field that split the Mn^{2+} levels in zero-applied magnetic field. The injection of a second exciton almost cancel the carriers Mn exchange interaction and the Mn spin splitting is significantly reduced. The fine structure of the biexciton transition reveals that the orbital carriers wave functions are slightly perturbed by the interaction with the magnetic ion.

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*Electronic address: lbseombes@spectro.ujf-grenoble.fr

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