Zero-field spin quantum beats in charged quantum dots

I. E. Kozin,[1,2] V. G. Davydov,[1] I. V. Ignatiev,[1,2] A. V. Kavokin,[3] K. V. Kavokin,[4] G. Malpuech,[3] Hong-Wen Ren,[1] M. Sugisaki,[1] S. Sugou,[1] and Y. Masumoto[1,5]

[1]*Single Quantum Dot Project, ERATO, JST, Japan*
[2]*Institute of Physics, St. Petersburg State University, St. Petersburg 198504, Russia*
[3]*LASMEA, Université Blaise Pascal-Clermont-Ferrand II, 63177 Aubière Cedex, France*
[4]*Ioffe Physico-Technical Institute, 26 Politekhnicheskaya, St. Petersburg 194021, Russia*
[5]*Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan*

Spins of resident electrons in charged quantum dots (QD's) act as local magnets inducing the Zeeman splitting of excitons trapped into dots. This is evidenced by the observation of quantum beats in the linearly polarized time-resolved photoluminescence of a biased array of self-assembled InP QD's. An external magnetic field is found to shorten the spin beats' decay time keeping constant the frequency of the beats. A model using the pseudospin formalism allows one to attribute the observed quantum beats to the radiative decay of hot trions having two electrons that occupy different energy levels in a QD.

The charged quantum dot (QD) is a peculiar quantum object exhibiting quite unusual optical properties.[1–7] If the neutral QD is an analog of an atom, the charged QD is an analog of an ion.[5] One should expect drastic alterations in the fine structure of the energy levels due to charging of the QD. Since the first observation of charged excitons in QD's,[1] they were studied in QD's with the electronic population controlled either by optical pumping[4] or by applying a bias.[3,6,7] The fine structure of charged excitons was studied by single-dot optical spectroscopy,[2–6] including experiments in magnetic fields.[2,5]

While the energy structure of QD's has been intensively studied, much less is known about coherent phenomena in QD's.[8–11] To the best of our knowledge, no experimental observations of coherent phenomena in charged QD's have been reported so far.

Here, we report on a new spin-related effect in charged QD's. We have observed spin quantum beats (QB's) in the *linearly polarized* photoluminescence (PL) of an InP QD ensemble under linearly polarized excitation, while circular-polarized components of PL under circular-polarized excitation have shown almost no modulation. This behavior cannot result from the splitting of excitonic levels into states corresponding to linear oscillators, such as those observed in Ref. 11. But it is typical for a Zeeman doublet which is split by a magnetic field. In our case, such a Zeeman-like splitting is observed in the absence of an external magnetic field. Moreover, an applied magnetic field suppresses the QB's caused by this splitting. We attribute this unexpected behavior to the peculiar spin structure of the three-particle complex (trion) formed by an excess (resident) electron located in the QD and a photocreated electron-hole pair.

We have studied heterostructures with single layers of InP self-assembled QD's embedded between $Ga_{0.5}In_{0.5}P$ barrier layers grown by gas-source molecular-beam epitaxy. The average diameter of QD's was about 40 nm with a height of about 5 nm. The details of the growth procedure and of the sample characterization are reported elsewhere.[12] In order to control the charge of QD's, a semitransparent Shottky con-

tact has been fabricated on the top surface of the sample, and an ohmic contact has been attached onto the back surface. The total thickness of the undoped layers was about 0.5 μm. The PL was excited within the PL band of the QD's by $(2-4)$-ps pulses of a mode-locked Ti:sapphire laser, and detected at the selected energies near the maximum of the PL line [see inset in Fig. 1(a)] with a time resolution of 6 ps, using a 0.25-m subtractive-dispersion double monochromator and a streak camera. The measurements were done in linear and circular polarizations under normal light incidence. The temperature of the sample was 5 K.

Figure 1(a) shows the time-resolved PL kinetics excited by the linearly polarized light, and detected in the same (further referred to as parallel) linear polarization. The PL tran-
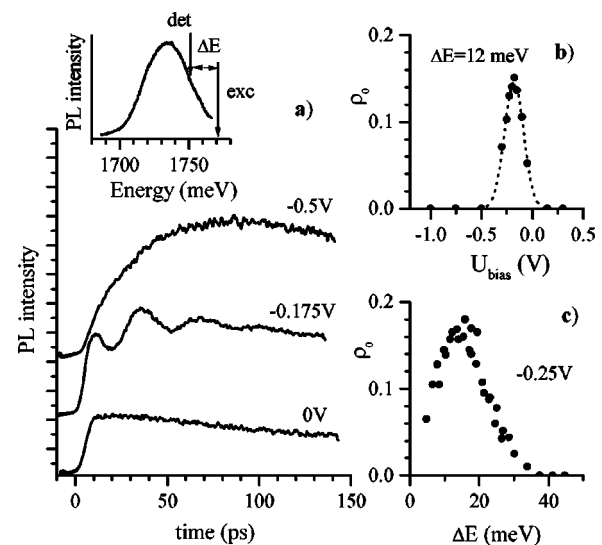

FIG. 1. (a) PL kinetics of the InP QD's in the linear polarization parallel to that of excitation at the spectral point, with Stokes shift between the excitation and detection energies of $\Delta E = 12$ meV for different bias. (b) Bias dependence of the QB amplitude ρ_0. Dashed line is the fit by a Gaussian with full width at half maximum $\Delta U = 0.22$ V. (c) QB amplitude ρ_0 versus the Stokes shift.
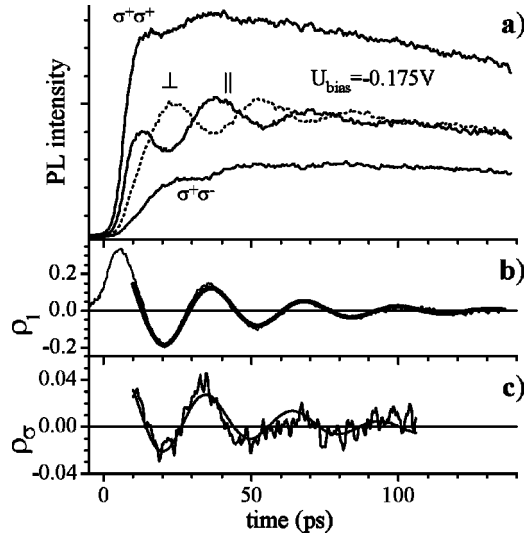
FIG. 2. (a) PL kinetics in the circular parallel ($\sigma^+\sigma^+$) and cross- ($\sigma^+\sigma^-$) polarizations, and also in the linear parallel ($\parallel$) and cross ($\perp$) polarizations. Applied bias $U_{bias} = -0.175$ V; Stokes shift $\Delta E = 15$ meV. (b) Degree of linear polarization ρ_l (noisy curve) and the fit (thick gray curve) by Eq. (1) with $\tau = 30$ ps, $\omega = 0.20$ ps^{-1}, and $\rho_0 = 0.2$. (c) Degree of circular polarization ρ_σ (noisy curve) and the fit (solid curve) by Eq. (1) with the same values of τ and ω and $\rho_0 = 0.05$. Non-oscillating part of ρ_σ is subtracted.

sients measured at the intermediate bias (of -0.175 V) show pronounced oscillations with a period of about 30 ps. Such oscillations are absent at zero electric field as well as in the strong-field limit [see Fig. 1(b)].

We assume that the oscillations appear in the case of optical excitation of the QD's containing *one* resident electron per dot. The presence of excess carriers in QD's under study at positive bias was evidenced in Refs. 15 and 16. The presence of the carriers can be easily checked by studying PL kinetics. Optical excitation creates an electron-hole pair in the excited state. The long rise time of the PL from the ground state of the electron-hole pair is governed by the relaxation time of the pair from the excited state and can be observed if there are no resident electrons in the QD's. This case is realized at strong negative biases as shown in Fig. 1(a). Extremely short rise times for small positive or zero bias evidence that, in this regime, the conduction-band ground state is occupied by an *extra electron* coming from the *n*-doped substrate or donors that are inevitably present in the system. At positive bias, each QD contains, on average, more than two resident electrons. Under strong negative bias, most of the dots are expected to be neutral, because of their field-induced depletion. The unusual QB's are observed at an intermediate negative bias [see Fig. 1(b)] where about a quarter of the QD's have single resident electrons, as will be shown below.

Figure 2(a) shows the time-resolved PL measured in the intermediate-field regime (bias of -0.175 V). The magnetic field is always zero. After excitation by a circularly polarized light (σ^+) and detection either in σ^+or in σ^- circular polarizations, we observe oscillations whose amplitude is quite weak compared to the value of the background signal in σ^+
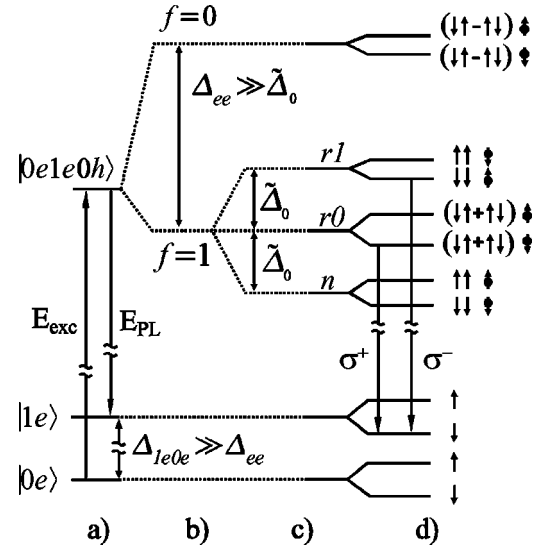

FIG. 3. Scheme of the optical transitions in a charged QD. The upper group of levels ($|0e1e0h\rangle$) represent the fine structure of a hot trion. Levels $|0e\rangle$ and $|1e\rangle$ are the states of the QD before absorption and after emission of a photon, respectively. $\uparrow$ and $\Updownarrow$ indicate the electron and hole spins, respectively.

polarization. The PL excited by linearly polarized light exhibits pronounced oscillations having opposite phases in parallel and cross polarizations (the cross polarization is orthogonal to the polarization of the incident light). These oscillations clearly manifest QB's between two eigenstates of the system corresponding to circularly polarized optical transitions. Fig. 2(b) shows the linear polarization degree of the PL: $\rho_l = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the PL intensities on the parallel and cross polarizations, respectively. It exhibits pronounced oscillations without any constant background, which can be well fitted by a function

$$\rho(t) = \rho_0 \exp(-t/\tau)\cos(\omega t), \qquad (1)$$

where ρ_0, τ, and ω are fitting parameters. Amplitude of the QB's, ρ_0, is sensitive to the applied bias and to the shift between the energies of excitation and detection of the PL, as shown in Figs. 1(b) and 1(c), respectively.

The combination of a nearly constant circular polarization of PL under circularly polarized excitation and pronounced beats in linear polarizations is usually a signature of the Zeeman splitting of σ^+ and σ^- polarized exciton states (to fit our experimental curves, a splitting of 0.12 meV would be required). We attribute the surprising Zeeman-like exciton splitting in the absence of an external magnetic field to the effect of *internal* exchange fields created by resident electrons in QD's.

We assume that a QD contains a resident electron in its ground state $|0e\rangle$. Optical excitation creates a hole in the ground state $|0h\rangle$ and an electron in the excited state $|1e\rangle$.[13] Under these conditions, the QD passes into the state $|0e1e0h\rangle$ shown in Fig. 3(a), which is a hot trion state. We consider hereafter the fine energy structure of the hot trion, where spins of the photocreated and resident electrons can be

parallel or antiparallel. The cold trion, created after the relaxation of the photoexcited electron to its ground state, has a trivial fine structure consisting of a single Kramers doublet, because spins of two electrons at the same energy level should be antiparallel, forming a singlet state. It is clear, therefore, that the cold trion cannot be responsible for the observed QB's.

The trion lifetime in the excited state is governed by the electron relaxation time. QB's are observed at relatively small Stokes shifts $\Delta E < 30$ meV [see Fig. 1(c)], i.e., at energies of photocreated electrons (relative to their ground state), which are smaller than the LO phonon energy in the InP QD's, $E_{LO} = 45$ meV.[14] The only way for such an electron to relax is to emit an acoustic phonon. This process takes several tens of picosecond.[14] Therefore the QB's can be observed within this time. This conclusion is in a perfect agreement with the data [see Fig. 2(b)].

The fine energy structure of the trion is governed by the exchange interaction of three particles. The electrons, being identical particles, interact with each other much stronger than each of them interact with the hole. This interaction forms the energy spectrum consisting of a singlet ($f=0$) and a triplet ($f=1$), where $\vec{f} = \vec{s}_1 + \vec{s}_2$ is the total spin of the two electrons [see Fig. 3(b)]. One can assume that the singlet-triplet splitting Δ_{ee} in the InP QD's is of the same order of magnitude as that in the InAs QD's, where it has been estimated as 3.5 meV.[20]

The exchange interaction of an electron and a hole is well studied for excitons in quantum wells[17] and QD's.[18] It is known that the energy spectrum of the QD exciton consists of two doublets, one radiative and one nonradiative, with the splitting between them, Δ_0, of the order of 0.1 meV. The in-plane asymmetry of QD's results in the further splitting of the radiative doublet described by the parameter $\Delta_1 \ll \Delta_0$. The splitting of the nonradiative doublet, Δ_2, is much weaker. Since $\Delta_{ee} \gg \Delta_0$, one can consider the exchange interaction of the hole with two electrons in a trion as an interaction of the hole angular momentum $\vec{J}$ with the total spin of the two electrons $\vec{f}$. This is most conveniently done by choosing the spin states with $J_z = |+3/2\rangle$ and $J_z = |-3/2\rangle$ of the hole for the basic states of a pseudospin $j=1/2$, which we denote as $|-1/2\rangle$ and $|+1/2\rangle$, respectively.[17] Using the exciton pseudospin Hamiltonian from Ref. 17, we obtain

$$\hat{H}^{ex}_{hee} = 2\tilde{\Delta}_0 f_z j_z + \tilde{\Delta}_1 (f_x j_x - f_y j_y) + \tilde{\Delta}_2 (f_x j_x + f_y j_y), \quad (2)$$

where $\tilde{\Delta}_{0,1,2} = (\Delta^{e1}_{0,1,2} + \Delta^{e2}_{0,1,2})/2$ and $\Delta^{ei}_{0,1,2}$ are the corresponding energy constants for the interaction of the hole with the ith electron.

A very essential point is that in Eq. (2) the heavy hole pseudospin $j=1/2$ interacts with an *integer* spin $f=0$, 1. As a result, the energy spectrum of the entire spin system obeys the Kramers theorem: in the absence of magnetic fields it consists of doublets which do not split further no matter how low the geometric QD symmetry becomes. The corresponding energy spectrum, shown in Fig. 3(c) for the case $\tilde{\Delta}_1 = \tilde{\Delta}_2 = 0$, governs the polarization dynamics of PL.

Since the energy separation between the $f=0$ and $f=1$ level groups is greater than the exciting-pulse bandwidth, they can be considered separately. The $f=0$ doublet can yield no beats; therefore the analysis below will be concentrated on the $f=1$ group of levels. In this group, there are two radiative doublets and a nonradiative one, marked in Fig. 3(c) by r_1, r_0, and n, respectively.

Depending on the initial spin state of the resident electron, s_z, the circularly polarized light excites different trion states:

$$s_z = +1/2, \quad \sigma^- \to |+1\rangle |+1/2\rangle, \quad \sigma^+ \to |0\rangle |-1/2\rangle, \quad (3)$$

$$s_z = -1/2, \quad \sigma^+ \to |-1\rangle |-1/2\rangle, \quad \sigma^- \to |0\rangle |+1/2\rangle. \quad (4)$$

Here we have used the pseudospin notation $|f_z\rangle |j_z\rangle$.

As seen from Eqs. (3) and (4), only one state of the radiative doublets r_0 or r_1 can be excited by the circularly polarized light. The linearly polarized laser light coherently excites two states, one of them belonging to the r_0 doublet, and the other one to the r_1 doublet. For the case of $s_z = +1/2$, these two excited states are marked in Fig. 3(d) by arrows which denote the radiative transitions from these states.[19] Due to the energy separation of r_0 and r_1 doublets, radiative transitions from these states excited coherently should give rise to QB's at the frequency $\omega = \tilde{\Delta}_0/\hbar$. We believe that the observed QB's result from this coherent process.

Averaging the intensities of the polarized components of light over the spin states of resident electrons in the ensemble of QD's, we obtain an expression for the linear polarization degree:

$$\rho_l(t) \approx 4/5 \cos(\omega t). \quad (5)$$

Equation (5) predicts a considerably larger amplitude of the QB's, $\rho_0 = 0.8$, than the maximum of the experimentally observed value [$\rho_0 \approx 0.2$, see Figs. 1(b) and 1(c)]. The reduction of the beat amplitude is most likely caused by fluctuations in the occupancy of the QD's by resident electrons. The QD's containing no electron, or two electrons, evidently
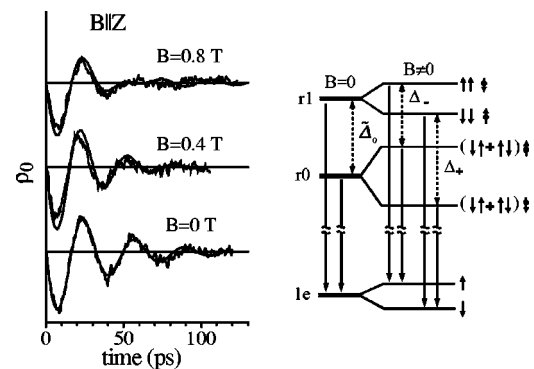

FIG. 4. QB's of trions (noisy curves) in magnetic field indicated against each curve and the fit (smooth curves) by function $\rho_l(B) = \rho_0 \exp(-t/\tau) \cos(\omega t) \cos(\Delta \omega t)$ with $\tau = 30$ ps, $\omega = 0.20$ ps^{-1}, and $\Delta \omega = g \mu_B B/\hbar$, where $g = 0.3$, for all the experimental curves. The scheme illustrates the difference of the beat energies, Δ_- and Δ_+, in a magnetic field for spin $\uparrow$ and $\downarrow$ of the resident electron.

should not contribute to the beat signal, but they do contribute to the total PL signal, thus reducing the amplitude of the oscillating polarization degree.

A similar analysis can be done if an in-plane anisotropy is present. Coupling between the two radiative doublets, induced by the $\tilde{\Delta}_1$ term in Eq. (2), makes the polarization of corresponding radiative states slightly *elliptical*. Under these conditions, the circularly polarized light excites coherently both radiative doublets, resulting in the small-amplitude beats upon a constant background: $\rho_\sigma \approx 1 - 2\alpha^2[1 - \cos(\omega t)]$, where $\alpha \approx \tilde{\Delta}_1/\tilde{\Delta}_0$.

One can see that the proposed model describes all the main qualitative features of the observed effect, namely, the QB's both in linear and circular polarizations at the same frequency, and the fact that the circular QB's are much weaker and are superimposed on a virtually time-independent background [see Figs. 2(b) 2 and 2(c)].

The model predicts also that the observed frequency of beats should not be sensitive to weak magnetic fields applied in the Faraday geometry (along z axis). Indeed, the magnetic field splits the Kramers doublets as shown in the scheme in Fig. 4.[21] The energy separation between the optically excited states, $\tilde{\Delta}_0$, depends on the spin projection of the resident electron onto the magnetic field. For one projection (say ↑), $\tilde{\Delta}_0$ is *increased* by the value $\hbar\Delta\omega$, and for another projection (↓) it is *decreased* by the same value, i.e. $\Delta_\pm = \tilde{\Delta}_0 \pm \hbar\Delta\omega$. Here $\hbar\Delta\omega = |g_h + g_e|\mu_B B$, where g_e and g_h are g factors of the electron and the hole, respectively, μ_B is the Bohr magneton, and B is the magnetic field. As a result, the average QB frequency of an ensemble of the QD's with non-polarized resident electrons is not shifted. While $\Delta\omega < 1/\tau$, the splitting results in an effective broadening of the frequency bandwidth of oscillations, which manifests itself in a more rapid damping. As seen from Fig. 4, the experimental polarization transients are well modeled by the calculations assuming $|g_h + g_e| \equiv g = 0.3$.

In conclusion, we have observed quantum beats with unusual polarization properties in the PL of InP QD's. The beats are shown to result from the peculiar spin structure of a hot trion formed by the electron-hole pair created by light and a resident electron.

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