Hole spin quantum beats in bulk ZnO

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We report on experimental investigations of the hole spin coherence in ZnO by time-resolved optical orientation experiments in a magnetic field perpendicular to the growth direction. We observe periodic oscillations of the circular polarization of the donor-bound-exciton luminescence in both ZnO epilayer and nonintentionally doped bulk ZnO. The measurement of these quantum beats, which originate from the Larmor precession of hole spins, yields an accurate determination of the transverse Landé g factors of the hole in both the ground and excited states of the donor-bound-exciton complex.

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I. INTRODUCTION

As a bright emitter in the short-wavelength range, wide band gap oxide semiconductor ZnO has raised renewed interest in the optoelectronic field. ZnO has also been proposed recently as a potential candidate for spintronic applications, thanks to its small spin-orbit coupling.[1,2] However, the electronic and excitonic structures of bulk ZnO have been debated for a long time and, compared to other major III-V and II-VI semiconductors, only few measurements of the carrier spin relaxation or coherent spin dynamics in bulk or even nanostructured ZnO have been published to date.[3–7] To the best of our knowledge, hole spin quantum beats have never been observed in ZnO.

In the wurtzite phase, the hexagonal crystal field and the spin-orbit effect give rise to three doubly-degenerated valence bands at the Brillouin-zone center: labeled A, B, and C. At low temperature, the photoluminescence spectra are dominated by a large number of bound-exciton complex lines, mainly associated to donor impurities even in nonintentionally doped ZnO. Since those complexes consist of a singlet of electrons and an unpaired hole, the spin properties of the complex are directly linked to the orientation of the localized hole.[8] In a previous paper,[7] we have investigated the hole spin lifetime T_1 localized in donor-bound-exciton complexes in the absence of external magnetic fields. Here, we report on the measurement of the hole spin coherence time T_2 and the Landé g factor in these complexes by studying the hole spin quantum beats (QBs) in bulk and epilayer ZnO samples in a transverse magnetic field.[9] Compared to magneto-optical experiments performed in the spectral domain, this time-resolved technique allows us to measure with great accuracy the absolute value of the effective hole g factor.[10,11]

The paper is organized as follows. Section II describes the ZnO samples and the time-resolved photoluminescence (PL) setup. Section III presents the experimental results we obtained on the measurement of hole spin quantum beats under the selective excitation of a donor-bound complex via one of its excited states. In Sec. IV, we describe and discuss the rate equation model we have developed to fit the experimental results and extract the hole spin coherence time and g factors.

II. SAMPLES AND EXPERIMENTAL SETUP

The samples under investigation have been grown by two different methods. Sample I is a high quality nominally undoped 1.1 μm thick epilayer grown on a α-sapphire (0001) substrate using an rf-plasma-assisted molecular beam epitaxy (MBE) system.[12] Sample II consists of a commercial bulk ZnO substrate of which surface crystal quality was improved using an O-plasma treatment. In the time-resolved PL experiments, the excitation source is a mode-locked frequency-doubled Ti:Sa laser with a 1.5 ps pulse width and a repetition frequency of 80 MHz. The laser beam propagating along the growth c axis is focused onto the sample to a 100 μm diameter spot with an average power $P_{\mathrm{exc}}=0.5$ mW.[13] The PL intensity is dispersed by an imaging spectrometer with a spectral resolution of 0.5 meV. The temporal and spectral properties of the signal are recorded by a S20 photocathode streak camera with an overall time resolution of 5 or 8 ps, depending on the considered time scale. The excitation laser is circularly polarized (σ^+) and the resulting PL circular polarization P_c is calculated as $P_c=(I^+-I^-)/(I^++I^-)$. Here, I^+ and I^- are the PL intensity components copolarized and counter polarized to the (σ^+) excitation laser. Magnetic fields are applied perpendicularly to the growth axis and are provided by permanent magnets (B up to 0.75 T) at a temperature of 16 K. Higher magnetic-field strengths up to 3.50 T are obtained at $T=1.7$ K via a superconductor coil. The time-resolved experimental method used here is based on tracing spin quantum beats that have their origin in the Larmor precession of spins in an external magnetic field. From the oscillation pulsation ω, the effective g factor can be deduced given that $\omega=g\mu_B B/\hbar$. The limitation of the spin QB technique is that the carrier spin-relaxation time has to be longer than the beat period since the QBs manifest as oscillations in the intensity of the polarized luminescence components.

III. EXPERIMENTAL RESULTS

The ZnO luminescence of samples I and II [Figs. 1(a) and 1(b), respectively] is characterized by a rich structure of excitonic lines in which previous studies[7] have allowed us to

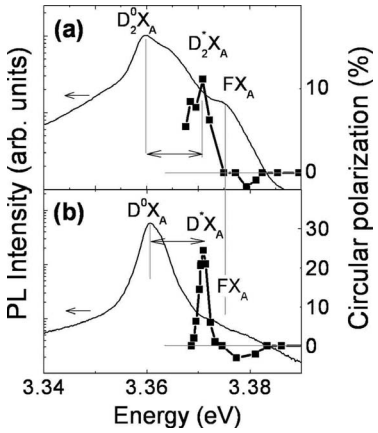

FIG. 1. Photoluminescence spectra at $T=16$ K of (a) sample I and (b) sample II. The degree of circular polarization (full square) as a function of excitation energy is also plotted when detecting on the $D_2^0X_A$ line (sample I) and on the D^0X_A line (sample II).

distinguish in sample I, the A free exciton emission line at $FX_A=3.375$ eV, and a line, labeled $D_2^0X_A$, associated to excitons bound to a neutral donor at 3.359 eV.[14–17] In sample II, a neutral donor-bound-exciton line, labeled D^0X_A, is identified at 3.361 eV. Figure 1 also displays the measured degree of PL circular polarization following a circularly polarized (σ^+) excitation at various energies when the detection is fixed on the $D_2^0X_A$ or D^0X_A energy position for samples I and II, respectively. A maximum degree of polarization is measured when the excitation energy is tuned at 11 meV (10 meV) above the $D_2^0X_A$ of sample I (D^0X_A of sample II). It corresponds to the selective excitation of an excited state (D^*X_A) of the neutral donor-bound exciton which allows to preserve the spin orientation during the relaxation to the ground state.[7] Moreover, as the total electron spin of the ground-state donor-bound exciton is zero, the measured PL circular polarization corresponds directly to the hole spin polarization. From time-resolved experiments at $B=0$ T [Figs. 2(a) and 3(a)], we have a direct measurement of the hole spin-relaxation time $T_1\sim350$ ps in sample I (at $T=16$ K) and $T_1\sim100$ ps in sample II (at $T=1.7$ K).

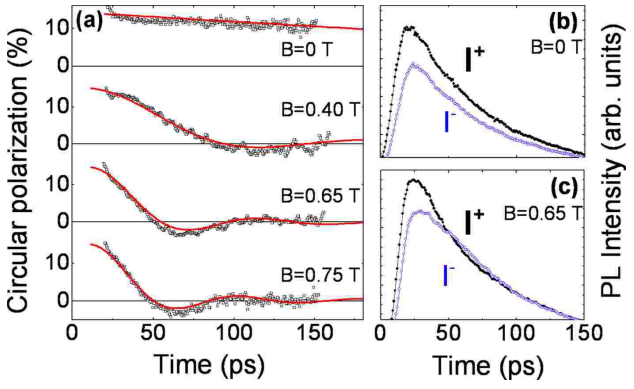

FIG. 2. (Color online) (a) Time evolution of the luminescence circular polarization in sample I for different magnetic-field values at $T=16$ K. The full lines correspond to the fit with the model presented in the text. (b) and (c) Time evolution of the PL circular components I^+ and I^- for $B=0$ and $B=0.65$ T, respectively.

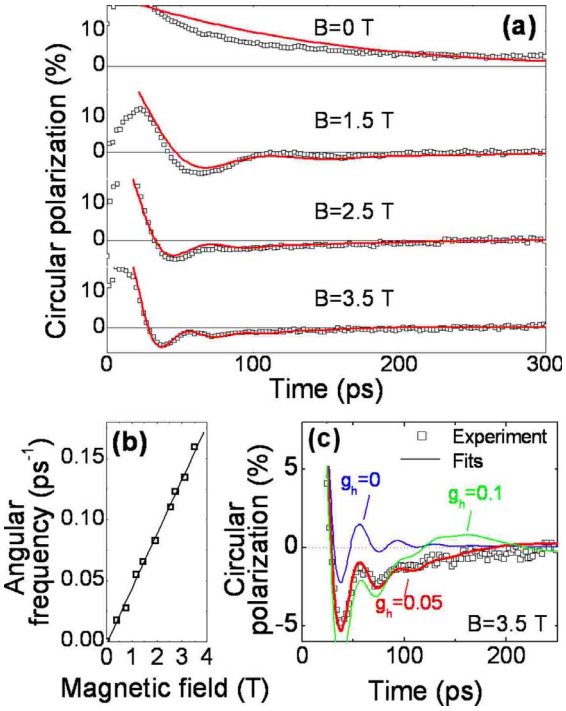

FIG. 3. (Color online) (a) Time evolution of the luminescence circular polarization in sample II for different magnetic-field values at $T=1.7$ K. The full lines correspond to the fits with the model presented in the text. (b) Dependence of the measured Larmor pulsation Ω of the PL quantum beats as a function of the magnetic field; the line is a linear fit. (c) Fits of the circular polarization dynamic at $B=3.5$ T for different values of g_h.

Under transverse magnetic fields, we observe oscillations of the luminescence polarization that arise from the oscillations of the luminescence components I^+ and I^- with a relative phase shift of π [see Fig. 2(c) for sample I]. To reduce the uncertainties on the determination of the resulting g factor, we have recorded the time evolution of the luminescence circular polarization at different magnetic-field strengths for the two samples. The results are displayed in Figs. 2(a) and 3(a). We note that the beat pulsation observed in both samples depends linearly on the magnetic-field strength [see Fig. 3(b) for sample II]. A simple analysis yields a g factor of 1.2 in sample I and 0.5 in sample II. Note that the asymmetry of the circular polarization oscillations in sample II under strong magnetic fields suggests the presence of a second oscillating period, difficult to resolve, that we will discuss later.[18]

We emphasize that the observed beats do not correspond to the well-known Larmor precession of electron spin since the measured beat pulsation is much smaller than the pulsation $\omega_e=g_e\mu_B B/\hbar$, already observed in n-doped ZnO with $g_e=1.96$.[3,6] As the detected luminescence in Figs. 2 and 3 arises from exciton bound to donors, we consider that the observed spin quantum beats arise from the Larmor precession of hole spins.

The hole transverse g factor in bound-exciton complexes in ZnO has been analyzed by magneto-optical experiments that measure the Zeeman energy splitting under transverse magnetic fields.[15,19,20] These data show that g_h lies in the

range $\sim 0.08 \pm 0.04$ for any neutral-donor-bound exciton considered.[20] Such a small value of g_h, which is consistent with the wurtzite crystal symmetry of ZnO, would require high magnetic fields to observe QBs. However, on sample I, we observe clear QBs at magnetic fields as low as 0.4 T yielding a g factor around ~ 1.2. This means that the measured QBs cannot be directly assigned to the Zeeman splitting of the ground state of the neutral-donor-bound exciton level and that we have to consider the role of the excited bound exciton D^*X_A which is initially photogenerated.

The excited state of the donor-bound exciton is linked to an excited state of the hole in the complex, as already observed by Puls *et al.*[21] in CdS. These authors studied the excited states of excitons bound to neutral impurities by excitation spectroscopy in CdS single crystals. Very similar excitation spectroscopy experiments were performed by Gutowski *et al.*[22] in ZnO under magnetic fields. They found a series of resonance peaks at $\sim 10-15$ meV above the ground state of bound excitons[22] with g factors in the range 1.2–1.9 depending on the considered resonance and sample strain. This is consistent with our results found in sample I. We note, however, that Gutowski *et al.*[22] had ascribed the bound-exciton complex to an acceptor level, which has been more recently demonstrated from similar experiments to be associated to donors.[15,23]

To further discuss about the nature of the excited state D^*X, we can point out that Meyer *et al.*[24] recently evidenced a correlation between ionized- and neutral-donor-bound excitons. The ionized-donor-bound exciton (D^+X) is located at $\sim 10-12$ meV above the ground state of the D^0X, i.e., in the same energy range of the considered excited state. However, since D^+X consists of one electron and one hole bound in the ionized-donor potential, the strong electron-hole exchange interaction (~ 1 meV in ZnO) should make the D^+X level insensitive to the small applied transverse magnetic field.[25] Finally, an excited state of D^0X built with the triplet state of the electron pair could also be considered. Yet, again, the exchange interaction between the electron pair and the hole prevents the observation of QBs in low transverse magnetic field. Our results are therefore consistent with the photogenerated bound-exciton excited state D^*X being constructed with the two electrons in the fundamental singlet state and the hole in an excited state.

IV. DISCUSSION

An accurate determination of the transverse g factors of the hole excited state (g_{h^*}) and of the hole ground state (g_h) in the bound exciton requires a fitting procedure that takes into account the two exciton levels D^*X_A and D^0X_A. We use simple rate equations to characterize the evolution of the excited and ground-state bound-exciton populations and spin polarizations as a function of time and magnetic field. Our model, schematically illustrated in Fig. 4, considers the resonant excitation (from D^0 state) of the bound-exciton excited state D^*X_A with an excited hole g factor labeled g_{h^*} and an energy relaxation to the ground state D^0X_A with a characteristic time τ_c. The ground state is characterized by a hole g factor g_h and a radiative decay time[26] τ_r. The spin decay time

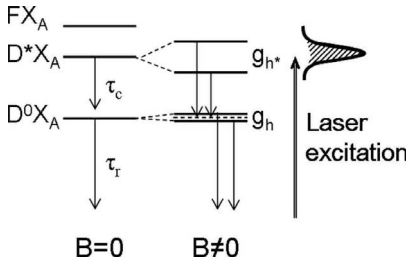

FIG. 4. Schematic representation of the levels and carrier paths considered by the model (see text).

of the hole in the excited (ground) state is given by τ_s^* (τ_s). We consider that the hole spin orientation is preserved during the energy relaxation from D^*X_A to D^0X_A.[27] We obtain[28]

$$\dot{n}^* = -\frac{n^*}{\tau_c} - \frac{n^*}{\tau_r^*},$$

$$\dot{n} = \frac{n^*}{\tau_c} - \frac{n}{\tau_r},$$

$$\dot{\vec{S}}^* = \vec{\Omega}^* \wedge \vec{S}^* - \vec{S}^*\left(\frac{1}{\tau_c} + \frac{1}{\tau_r^*} + \frac{1}{\tau_s^*}\right),$$

$$\dot{\vec{S}} = \vec{\Omega} \wedge \vec{S} + \frac{\vec{S}^*}{\tau_c} - \vec{S}\left(\frac{1}{\tau_s} + \frac{1}{\tau_r}\right), \tag{1}$$

where n (n^*) is the neutral (excited) bound-exciton population and $\vec{S}(\vec{S}^*)$ is the ground state (excited) exciton pseudospins; Ω and Ω^* are the precession frequencies of the hole ground and excited states, respectively. In a transverse magnetic field $\vec{B}=(B,0,0)$, the precession frequency writes $\Omega^{(*)}=g_{h^{(*)}}\mu_B B/\hbar$. Both τ_s^* and the recombination time of the excited state τ_r^* will be omitted in the following since they are assumed to be longer than the relaxation time τ_c.

The growth direction (Oz) is taken as the quantization axis. PL optical pumping experiments give access to the spin projection S_z along the growth direction. The differential equation system is analytically resolved and gives

$$n(t) = \frac{n^*(0)}{1 - \frac{\tau_c}{\tau_r}}(e^{-t/\tau_r} - e^{-t/\tau_c}),$$

$$S_z(t) = \frac{S_z^*(0)}{\left(1 - \frac{\tau_c}{\tau_s} - \frac{\tau_c}{\tau_r}\right)^2 + \tau_c^2(\Omega^* - \Omega)^2}\left[\left(1 - \frac{\tau_c}{\tau_s} - \frac{\tau_c}{\tau_r}\right)\right.$$
$$\times (e^{-(1/\tau_s + 1/\tau_r)t}\cos\Omega t - e^{-t/\tau_c}\cos\Omega^* t)$$
$$\left. - \tau_c(\Omega^* - \Omega)(e^{-(1/\tau_s + 1/\tau_r)t}\sin\Omega t - e^{-t/\tau_c}\sin\Omega^* t)\right]. \tag{2}$$

Note that for the sake of simplicity, $S^*(0)=15\%$ [$S^*(0)=22\%$] directly takes into account the spin losses during the generation or capture processes in sample I (sample II). τ_c

and τ_r are directly measured from the rising and decay times, respectively, of the total PL intensity of the ground state of the bound-exciton line. We found $\tau_c \sim 35$ ps for both samples and $\tau_r = 60$ ps for sample I and $\tau_r = 160$ ps for sample II. We have checked that the applied magnetic field does not modify these values.

The fitting parameters are the two-hole g factor values (g_h and g_{h^*}) and the spin decay time τ_s of the hole ground state. At zero magnetic field, τ_s corresponds to the spin-relaxation time T_1 of the hole ground state, directly extracted from the time evolution of the circular polarization at $B=0$. The presence of a magnetic field along (Ox) makes the hole spin precesses in the (yOz) plane, perpendicular to the magnetic field, leading to consider τ_s as the hole spin coherence time T_2 at $B \neq 0$.

For the QBs measured in sample I under low magnetic fields ($B < 1$ T in Fig. 2), the contribution of g_h is negligible. The fitting procedure illustrates that the QBs measured on the luminescence of the ground-state bound exciton are dominated by the beating pattern induced by the Zeeman splitting of the excited hole spin states. The damping of the oscillations is then mainly governed by τ_c that corresponds to the energy relaxation time of the excited hole. The contribution of τ_s on the shape of the curves is only weak, leading us to consider that $\tau_s > \tau_c$. Therefore, the observed dependence of the circular polarization decay with the applied magnetic field in Figs. 2(a) and 3(a) is thus not due to a magnetic field induced τ_s dependence on the hole ground state; it is simply related to the special features associated to the photogeneration or relaxation processes on the exciton bound to donors.

As shown on Fig. 2(a), a good agreement between the fitting and experimental data in sample I is achieved with $g_{h^*} = 1.25 \pm 0.02$ and $\tau_s \equiv T_2$ in the range 100–350 ps.

The fitting procedure of the QBs observed in sample II under stronger magnetic fields ($B > 1.5$ T) demonstrates that both g factors of the excited and ground states of the donor-bound-exciton complex have to be taken into account. At low magnetic field ($B < 1$ T),[29] the role of g_h is negligible, as in sample I. Under higher magnetic fields, the contribution of the spin quantum beats from the hole ground state is evidenced by the asymmetry of the circular polarization oscillations. Figure 3(c) clearly illustrates the impact of the value of g_h that is no longer negligible to correctly fit the measured circular polarization at $B = 3.5$ T. Thus, the fitting parameters g_{h^*}, g_h, and τ_s are extracted with a good accuracy. We find $g_{h^*} = 0.55 \pm 0.02$, $g_h = 0.05 \pm 0.02$, and $\tau_s \equiv T_2$ in the range 80–100 ps.

The difference between the two measured values of g_{h^*} in the two samples can be explained by the high sensitivity of the exciton bound to donor complexes to the electronic structure. The presence of residual strain, the chemical nature of the donor considered, the contribution of the different excitonic lines, as well as the possible contribution of holes from the B valence band highly impact the electronic environment of the hole wave function. This is further supported by the fact that different values for the hole spin-relaxation time T_1 have also been measured.

Finally, the measured T_2 value in bulk ZnO is comparable to the hole spin coherence time found in GaN bulk material[11] or in III-V semiconductor quantum well structures.[10,30]

V. CONCLUSION

In conclusion, we have performed time-resolved optical pumping experiments of bulk and epilayer ZnO in a transverse magnetic field. The observation of spin quantum beats allows us to measure with good accuracy the transverse hole g factor of the neutral-donor-bound exciton $g_h \sim 0.05 \pm 0.02$. Since the excitation of the donor-bound exciton is provided via the selective excitation of one of its excited state, the observed spin quantum beats are also highly influenced by the g factor of this excited state. From these time-resolved experiments, we measured the spin coherence time of the localized hole which is about $T_2 \sim 100$ ps in bulk ZnO.

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