Efficiency of optical spin injection and spin loss from a diluted magnetic semiconductor ZnMnSe to CdSe nonmagnetic quantum dots

D. Dagnelund, I. A Buyanova, and W. M. Chen
Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden

A. Murayama, T. Furuta, K. Hyomi, I. Souma, and Y. Oka
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
(Received 23 August 2007; published 31 January 2008)

Magneto-optical spectroscopy in combination with tunable laser spectroscopy is employed to study optical spin injection from a diluted magnetic semiconductor (DMS) ZnMnSe into nonmagnetic CdSe quantum dots (QDs). Observation of a DMS feature in the excitation spectra of the QD photoluminescence polarization provides clear evidence for optical spin-injection from the DMS to the QDs. By means of a rate equation analysis, the injected spin polarization is deduced to be about 32% at 5 T, decreasing from 100% before the injection. The observed spin loss is shown to occur during the spin injection process including crossing the heterointerfaces and energy relaxation within the QDs.

DOI: 10.1103/PhysRevB.77.035437 PACS number(s): 72.25.−b, 78.67.Hc, 78.55.Et

While conventional electronics rely on a controlled manipulation of charge only, future generation devices are expected to exploit the additional spin degree of freedom of charge carriers, promising faster, smaller, less power consuming, and nonvolatile devices.[1–3] The underlying research field of spintronics has been growing rapidly over the past years. Success of semiconductor-based spintronics relies *inter alia* on the ability to inject spin-polarized carriers or excitons into semiconductors, optimization of their spin lifetimes, coherent spin transport within a device, possibility to manipulate spin information in a controlled way, and reliable spin detection. Recent advances have demonstrated important steps toward implementation of these basic requirements. For example, efficient optical[4–11] and electrical[12–15] spin injections were achieved using a highly spin-polarized dilute magnetic semiconductor (DMS) as a spin aligner and a nonmagnetic layer as a spin detector. Semiconductor quantum dots (QDs) such as CdSe QDs are one of the most interesting candidates for quantum information processing and spin detection due to their predicted slow spin relaxation and decoherence as well as high efficiency of optical transitions. Unfortunately, the spin-injection process and physical mechanisms for spin loss in QD systems are still poorly understood.

The objective of this study is to examine optical spin injection from a ZnMnSe DMS to nonmagnetic self-assembled CdSe QDs by means of circularly polarized photoluminescence (PL) and tunable laser spectroscopy under magnetic fields. The ZnMnSe DMS layer was used as a source of spin-polarized excitons/carriers upon optical excitation. Direct evidence for subsequent exciton and spin injection into the CdSe QDs was provided by the observation of an excitation peak of the QD PL (intensity and polarization) at the energy of the DMS excitons. Our approach has also enabled us to separate the contribution of the spin injection from that of carrier/exciton transfer from the ZnSe layers and photogeneration within the QDs. From a detailed analysis of rate equations, we were able to precisely and reliably determine the spin-injection efficiency and the degree of spin loss during the injection process.

The sample structure studied in this work was grown by molecular beam epitaxy on a GaAs (100) substrate. A schematic picture of the structure is shown in the inset in Fig. 1. The $Zn_{0.80}Mn_{0.20}Se$ DMS layer with a thickness of 100 nm was grown on a ZnSe-buffer layer, followed by a spacer layer of ZnSe with a thickness of 10 nm. Then, three monolayers of CdSe were grown on the ZnSe spacer, forming self-assembled QDs. The dots were capped by a 20-nm-thick ZnSe layer. Spin polarization and spin-injection properties of the structure were studied by employing circularly polarized PL and tunable laser spectroscopy at 2 K and at magnetic fields up to 5 T. The excitation light provided by a dye laser was tuned in the range of 422–462 nm, with a spot size of about 1 mm and low excitation power (<50 mW). The direction of the propagating light was normal to the sample surface and parallel to the magnetic field for both excitation and detection. The excitation light was linearly polarized, unless specified. The detection energy during PL excitation (PLE) measurements by the tunable laser was set at 2.54 eV.

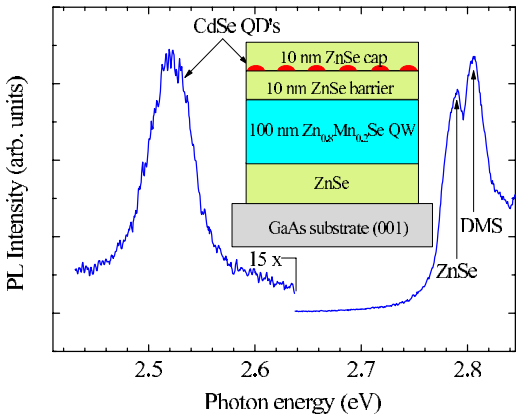

FIG. 1. (Color online) PL spectra of the studied structure where the PL peaks from the CdSe QD, the ZnMnSe DMS, and the ZnSe are clearly resolved. The spectra are taken at 0 T and 2 K. PL was excited by linearly polarized light at 2.95 eV. The inset shows a schematic drawing of the studied structure.

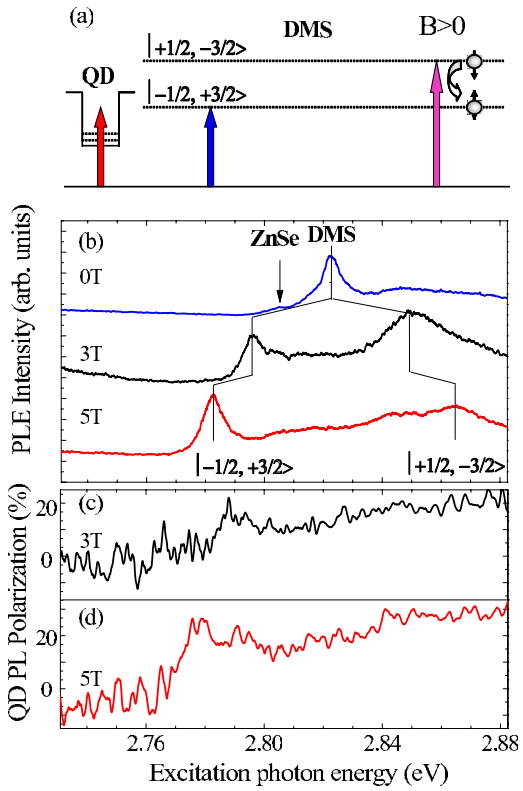

FIG. 2. (Color online) (a) A schematic picture of the optical excitation at 5 T. (b) Excitation spectra of the CdSe QD PL emission at 0, 3, and 5 T by linearly polarized laser light. The total intensity of the high-energy QD was selectively detected by setting the detection photon energy at 2.54 eV. [(c) and (d)] The polarization degree $[P_0=(\sigma^+-\sigma^-)/(\sigma^++\sigma^-)]$ of the QD PL at 2.54 eV as a function of excitation photon energy by linearly polarized laser light at 3 and 5 T.

The PL signal was analyzed by a grating monochromator and was detected by either a photomultiplier tube or a charge coupled device camera.

Figure 1 shows a typical PL spectrum at 0 T. Both CdSe QDs and ZnMnSe DMS give rise to strong PL, with the two PL peaks clearly resolved. The lowest-energy PL emission (peaking at around 2.52 eV) originates from the quantum confined exciton ground state transition in the CdSe QDs, confirmed by the observation of sharp PL lines from individual dots in micro-PL measurements on a reference QD sample without the DMS. The highest-energy PL peak (at 2.81 eV) is associated with ZnMnSe heavy hole excitons accompanied by a PL peak at 2.79 eV from ZnSe. The broad excitonic emission band of the QDs is due to inhomogeneity in the size and composition of the QDs ensemble in the system. In the absence of an external magnetic field, the two oppositely circular polarizations are equal in intensity due to spin degeneracy of the ground state, leading to unpolarized PL emission from both QDs and DMS (not shown in Fig. 1).

In order to obtain detailed information on the spin- and exciton/carrier-injection processes, tunable optical excitation of the QD PL emission was employed [see Figs. 2(a) and 2(b)]. Several regions of the PLE spectra, related to preferential light absorption within different spatial regions of the structure, can be distinguished [Fig. 2(b)]. Photoexcitation with photon energies below 2.76 eV corresponds to resonant absorption within the CdSe QDs. The excitonic absorption within the nonmagnetic ZnSe layer gives rise to the PLE peak at ~2.805 eV. Moreover, a pronounced PLE peak can be seen at, e.g., 2.82 eV at 0 T, which originates from the lowest exciton states $|-1/2, +3/2\rangle$ and $|+1/2, -3/2\rangle$ of the DMS. As expected from the strong exchange interaction between carriers and Mn^{2+} ions,[16] the DMS peak exhibits a giant Zeeman splitting into two components in an applied magnetic field [Fig. 2(b)]. This splitting corresponds to the Zeeman splitting of the two exciton states, leaving the σ^+-active $|-1/2, +3/2\rangle$ state lower in energy. This is confirmed by the performed PLE measurements at 5 T using circularly polarized excitation light, where the low and high components of the DMS peaks can only be excited using the σ^+ and σ^- light polarization, respectively (not shown in Fig. 2). The intensity of the DMS-related PLE peaks is about ten times higher than that of the resonant excitation of the QDs with photon energy below the DMS band gap. This indicates that about 90% of the excitons participating in QD recombination are injected from the DMS when the excitation energy is tuned resonant with the DMS exciton energy, thus providing unambiguous proof for efficient exciton/carrier injection from the DMS to the QDs.[17]

In order to evaluate spin-injection efficiency from the DMS to the QDs, the polarization degree of the QD's PL [i.e., $P_0=(\sigma^+-\sigma^-)/(\sigma^++\sigma^-)$] as a function of excitation photon energy was studied in detail and is shown in Figs. 2(c) and 2(d). P_0 is determined by the spin polarization degree P of the excitons in the QDs given by

$$P_0 = P \equiv \frac{N_+^{QD} - N_-^{QD}}{N_+^{QD} + N_-^{QD}}, \tag{1}$$

where N_+^{QD} (N_-^{QD}) is the number of the σ^+-active $|-1/2, +3/2\rangle$ exciton (σ^--active $|+1/2, -3/2\rangle$ exciton) in the QDs. Apparent from Figs. 2(c) and 2(d), QD PL polarization strongly depends on the excitation energy, reflecting in what region of the studied structure spins were created. Resonant excitation below the DMS and ZnSe excitonic band gap energies provides a means to probe the spin polarization properties of the QDs alone. As expected, the "intrinsic" QD polarization degree [e.g., $P\sim-5\%$ at 5 T, Fig. 2(d)] is negative. This is determined by the ordering of the spin levels in the QDs, i.e., the σ^--active exciton state lies lower in energy due to Zeeman splitting and is thus favorably populated. When the excitation light was tuned resonant with the σ^+ polarized DMS exciton state, a reversal in the QD PL polarization sign was detected, which can only be interpreted as a result of population inversion between the two spin sublevels in the QDs. This is achieved via the injection of excitons/carriers from the DMS and provides the experimental evidence for the spin injection from the DMS to the QDs. In addition, the PL polarization of the QDs remains almost unaffected even if we resonantly excite the σ^- DMS peak. This can be explained by an extremely fast spin-flip process in the DMS in comparison with the injection to the QDs, as illustrated in Fig. 2(a). Thus, the DMS acts as an effective spin

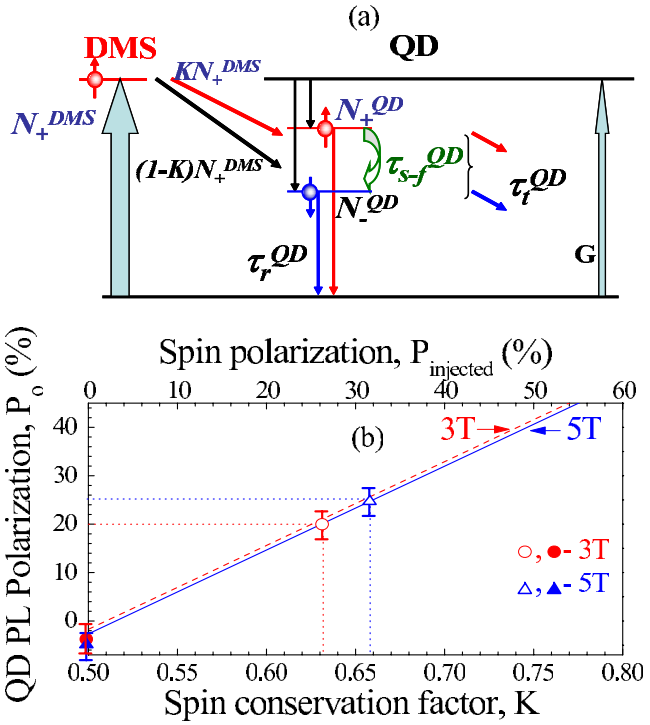

FIG. 3. (Color online) (a) A schematic picture of the spin injection, optical excitation, and recombination processes is shown. (b) PL polarization of the CdSe QDs as a function of the spin conservation factor K and the polarization of the injected spins P_{injected}. The open and filled circles are the experimentally determined values at 3 T, obtained when the excitation photon energy was tuned at and below the lowest exciton spin state of the DMS, respectively. The corresponding values at 5 T are shown by open and filled triangles. The vertical bars denote the experimental error bar. The dashed and solid lines indicate the simulated QD's polarization based on Eq. (3) at 3 and 5 T, respectively. The horizontal and vertical dotted lines are a guide to the eye.

filter, converting all σ^--active spins into σ^+-active spins. This is consistent with our previous results from the ZnMnSe DMS.[18–20] The degree of the QD PL polarization detected under resonant photoexcitation with either of the spin-split subbands of the DMS will thus reflect the spin-injection efficiency from the DMS to the QDs. In order to estimate the spin polarization degree of the excitons recombining in the QD and the extent of spin loss during the spin injection, a detailed analysis was performed using the following coupled rate equations under the condition of the resonant excitation by linearly polarized light at the lowest exciton spin state $|-1/2, +3/2\rangle$ of the DMS [Fig. 3(a)]:

$$\frac{dN_+^{QD}}{dt} = G + KN_+^{DMS} - \frac{N_+^{QD}}{\tau_r^{QD}} - \frac{N_+^{QD}}{\tau_t^{QD}} - \frac{N_+^{QD}}{\tau_{s-f}^{QD}(1+e^{-\Delta E/kT})} + \frac{N_-^{QD}}{\tau_{s-f}^{QD}(1+e^{\Delta E/kT})},$$

$$\frac{dN_-^{QD}}{dt} = G + (1-K)N_+^{DMS} - \frac{N_-^{QD}}{\tau_r^{QD}} - \frac{N_-^{QD}}{\tau_t^{QD}} + \frac{N_+^{QD}}{\tau_{s-f}^{QD}(1+e^{-\Delta E/kT})} - \frac{N_-^{QD}}{\tau_{s-f}^{QD}(1+e^{\Delta E/kT})}. \quad (2)$$

Such an excitation condition ensures that only σ^+-active exciton spins are generated, leading to a complete spin alignment in the DMS. This safely rules out an incomplete spin alignment in the DMS as a possible source of spin loss. Since the excitation photon energy is lower than that of the ZnSe excitonic band gap, a contribution from the ZnSe layer in the spin injection can also be neglected. The first two terms on the right hand side of Eq. (2) represent a direct generation of excitons within the QDs by laser light and feeding of the QDs from the DMS, respectively. N_+^{DMS} is the total number of the excitons injected from the DMS to the QDs. $K \equiv N_+^{\text{injected}}/N_+^{DMS}$ is a dimensionless factor describing the spin conservation of the injected excitons, where N_+^{injected} denotes the number of the injected excitons that still retain the σ^+ polarization. $K=1$ and $K=0.5$ represent the two extreme cases of complete spin conservation and total spin loss during the spin injection, respectively. The next two terms in Eq. (2) account for exciton recombination and interdot exciton transfer from the dots with higher exciton energies to the ones with lower energies when the polarization properties of the QD PL at the highest energy are analyzed here. The last two terms model the spin-flip process between the two spin sublevels of the QDs. τ_t^{QD}, τ_r^{QD}, and τ_{s-f}^{QD} represent interdot exciton transfer time, exciton recombination time, and exciton spin-relaxation time in the QDs. They have been independently determined in our time-resolved PL measurements: $\tau_t^{QD}=50$ ps, $\tau_r^{QD}=200$ ps, and $\tau_{s-f}^{QD}=800$ ps.[11,21] The Zeeman splitting between the spin levels in the QDs at 5 T is estimated to be $\Delta E=0.50$ meV from the Zeeman splitting observed in μ-PL experiments. kT denotes the thermal energy of the excitons. From this simple model, we were able to deduce an expression for the polarization of the QDs,

$$P = \underbrace{\frac{\frac{1-e^{\Delta E/KT}}{1+e^{\Delta E/KT}}\frac{1}{\tau_{s-f}^{QD}}}{\frac{1}{\tau_{s-f}^{QD}}+\frac{1}{\tau_r^{QD}}+\frac{1}{\tau_t^{QD}}}}_{\text{intrinsic}} + \underbrace{\frac{\frac{2K-1}{1+G/N_+^{DMS}}\left(\frac{1}{\tau_r^{QD}}+\frac{1}{\tau_t^{QD}}\right)}{\frac{1}{\tau_{s-f}^{QD}}+\frac{1}{\tau_r^{QD}}+\frac{1}{\tau_t^{QD}}}}_{DMS\text{-induced}}. \quad (3)$$

We can note that it contains two parts. The first part describes the intrinsic QD polarization, while the second one accounts for the spin injection from the DMS. The latter depends on K and the ratio between the direct photogeneration and the DMS pumping of the QDs. Results of the calculations are depicted in Fig. 3(b) where the QD PL polarization degree P_0 is plotted as a function of K. The calculated polarization degree ($P_0=-3\%$ at 5 T) at $K=0.5$, equivalent to the case without spin injection from the DMS, is in good agreement with the observed intrinsic QD polarization degree ($P_0=-5\%$). Furthermore, we can see that the experimentally obtained QD polarization degree of +25% at 5 T (upon the resonant excitation of the DMS $|-1/2, +3/2\rangle$ state)

yields $K \sim 0.66$. In other words, about 34% of the excitons lose their spin orientation during the spin injection. From this, the polarization of the injected excitons that reaches the QDs can be estimated as $P_{\text{injected}}=(N_{+}^{\text{injected}}-N_{-}^{\text{injected}})/N_{+}^{DMS}=2K-1=32\%$, decreasing from 100% in the DMS before the injection. At 3 T, $K \sim 0.63$ was estimated, which yields $P_{\text{injected}}=26\%$ [Fig. 3(b)].

There are several possible reasons for spin scattering during the spin injection, such as geometrical shape and size of the QDs, defects, roughness and potential of the interfaces along the path of the spin injection, and "unexpected" fast spin relaxation accompanying energy relaxation within the QDs. Previous studies of spin relaxation in similar QDs have revealed an important role of excited states in spin relaxation.[22,23] Unfortunately, the limited spectral range of our dye laser has prevented us from positively identifying any excited states of the QDs and their role in spin relaxation. However, we performed studies of spin injection as a function of magnetic field that can tune the energy of the lowest exciton state of the DMS, from which the spin injection is initiated, and, consequently, its energy separation from the QD exciton states. By lowering the energy of the $|-1/2, +3/2\rangle$ exciton state of the DMS by about 15 meV from 3 to 5 T [see Figs. 2(c) and 2(d)] a slight increase in the spin-injection efficiency was observed. This could hint at a possible role of energy relaxation within the QDs in spin loss. Considering the limited experimental accuracy and the limited tuning range of the DMS energy, however, no definite conclusion can be drawn at present. It should be noted that a similar or slightly higher spin-injection efficiency (20%–40%) was typically observed[4–11] for spin-injection from ZnMnSe to ZnCdSe quantum wells (QWs). Spin relaxation within the ZnCdSe QWs was shown from our earlier studies[24] to be rather fast, i.e., <20 ps at high K vector, 30 ps at small K, and 800 ps at $K=0$. As spin relaxation is generally expected to be slower in the QDs due to lack of exciton motion, the observation of similar spin-injection efficiency may hint that other sources of spin loss such as spin scattering by the interfaces and defects may play an important role during spin injection to the QDs. A detailed analysis of various possibilities for the observed limited spin-injection efficiency requires in-depth and systematic experimental studies of the effects of, e.g., interface properties, defects, energy relaxation process within the QDs, etc., as well as theoretical calculations, which are beyond the scope of this article. Nevertheless, we hope that the present work can stimulate further investigations to optimize spin-injection efficiency in semiconductor nanostructures.

In summary, by means of circularly polarized magneto-PL and tunable laser spectroscopy, we have provided unambiguous experimental evidence for optical spin injection from the ZnMnSe DMS to the CdSe QDs. A detailed analysis of the rate equations has enabled us to conclude that 66% of the injected spins retain their spin orientation at 5 T; i.e., 34% of them have lost their spin orientation during the spin injection. This resulted in only 32% of spin polarization when the injected spins reached the QDs, decreasing from the initial 100% in the DMS. Our results convincingly showed that the observed spin loss was not caused by an incomplete spin alignment in the DMS but due to severe spin scattering along the path of the spin injection and also possibly accompanying energy relaxation within the QDs. Further studies are required to identify the exact physical mechanisms for the observed spin loss, with the aim to improve spin injection efficiency.

Financial support by the Swedish Research Council (VR) and the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) is greatly appreciated. The authors would also like to thank the Ministry of Education, Science, and Culture, Japan, for its financial support.

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
[2] G. A. Prinz, Science **282**, 1660 (1998).
[3] Igor Žutić, Jaroslav Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[4] M. Oestreich, J. Hübner, D. Hägele, P. J. Klar, W. Heimbrodt, W. W. Rühle, D. E. Ashenford, and B. Lunn, Appl. Phys. Lett. **74**, 1251 (1999).
[5] I. A. Buyanova, I. G. Ivanov, B. Monemar, W. M. Chen, A. A. Toropov, Ya. V. Terent'ev, S. V. Sorokin, A. V. Lebedev, S. V. Ivanov, and P. S. Kop'ev, Appl. Phys. Lett. **81**, 2196 (2002).
[6] J. Seufert, G. Bacher, H. Schomig, A. Forchel, L. Hansen, G. Schmidt, and L. W. Molenkamp, Phys. Rev. B **69**, 035311 (2004).
[7] K. Kayanuma, M. C. Debnath, I. Souma, Z. Chen, A. Murayama, M. Kobayashi, H. Miyazaki, and Y. Oka, Phys. Status Solidi B **229**, 761 (2002).
[8] I. A. Buyanova, W. M. Chen, A. A. Toropov, S. V. Sorokin, S. V. Ivanov and P. S. Kop'ev, J. Supercond. **16**, 399 (2003).
[9] W. M. Chen, I. A. Buyanova, K. Kayanuma, K. Nishibayashi, K. Seo, A. Murayama, Y. Oka, A. A. Toropov, A. V. Lebedev, S. V. Sorokin, and S. V. Ivanov, Phys. Rev. B **72**, 073206 (2005).
[10] A. Murayama, T. Asahina, K. Nishibayashi, I. Souma, and Y. Oka, Appl. Phys. Lett. **88**, 023114 (2006).
[11] A. Murayama, T. Furuta, K. Hyomi, I. Suoma, Y. Oka, D. Dagnelund, I. A. Buyanova, and W. M. Chen, Phys. Rev. B **75**, 195308 (2007).
[12] R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, and L. W. Molenkamp, Nature (London) **402**, 787 (1999).
[13] Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature (London) **402**, 790 (1999).
[14] B. T. Jonker, Y. D. Park, B. R. Bennett, H. D. Cheong, G. Kioseoglou, and A. Petrou, Phys. Rev. B **62**, 8180 (2000).
[15] R. M. Stroud, A. T. Hanbicki, Y. D. Park, G. Kioseoglou, A. G. Petukhov, B. T. Jonker, G. Itskos, and A. Petrou, Phys. Rev. Lett. **89**, 166602 (2002).

[16] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).

[17] The exact physical process of the injection is currently unknown, as being exciton injection as a whole or subsequent injection of individual particles of the exciton.

[18] A. Murayama, K. Seo, K. Nishibayashi, I. Souma, and Y. Oka, Appl. Phys. Lett. **88**, 261105 (2006).

[19] W. M. Chen, I. A. Buyanova, G. Yu. Rudko, A. A. Toropov, Y. Terent'ev, S. V. Sorokin, A. V. Lebedev, S. V. Ivanov, P. S. Kop'ev, A. G. Mal'shukov, and K. A. Chao, Phys. Rev. B **67**, 125313 (2003).

[20] I. A. Buyanova, G. Yu. Rudko, W. M. Chen, K. Kayanuma, A. Murayama, Y. Oka, A. A. Toropov, S. V. Sorokin, and S. V. Ivanov, Phys. Rev. B **71**, 165203 (2005).

[21] The value of $\tau_r^{QD}=200$ ps was obtained by measuring the decay time of the lowest-energy QD excitons that do not suffer from an additional decay process by interdot exciton transfer. τ_t^{QD} was determined from the much shorter decay times observed from the high-energy QD excitons (as short as 50 ps at the highest energy), which is governed by interdot transfer to the lower-energy QD. τ_{s-f}^{QD} was determined by an analysis of the decay of the polarized PL arising from the two spin states of the QD excitons in an applied magnetic field. We note that the value of $\tau_{s-f}^{QD}=800$ ps is somewhat shorter than that reported for II-VI QD [e.g., S. Mackowski, T. A. Nguyen, H. E. Jackson, L. M. Smith, J. Kossut, and G. Karczewski, Appl. Phys. Lett. **83**, 5524 (2003); Yu. G. Kusrayev, A. V. Koudinov, B. P. Zakharchenya, S. Lee, J. K. Furdyn, and M. Dobrowolska, Phys. Rev. B **72**, 155301 (2005)], which we tentatively attribute to more severe spin scattering in the QDs studied in this work due to defects and interfaces.

[22] M. Scheibner, G. Bacher, S. Weber, A. Forchel, Th. Passow, and D. Hommel, Phys. Rev. B **67**, 153302 (2003).

[23] S. Mackowski, T. A. Nguyen, T. Gurung, K. Hewaparakrama, H. E. Jackson, L. M. Smith, J. Wrobel, K. Fronc, J. Kossut, and G. Karczewski, Phys. Rev. B **70**, 245312 (2004).

[24] W. M. Chen, I. A. Buyanova, K. Kayanuma, Z. H. Chen, A. Murayama, Y. Oka, A. A. Toropov, S. V. Sorokin, S. V. Ivanov, and P. S. Kop'ev, Appl. Phys. Lett. **85**, 5260 (2004).