Effect of spin-dependent Mn^{2+} internal transitions in $CdSe/Zn_{1-x}Mn_xSe$ magnetic semiconductor quantum dot systems

S. Lee*
Department of Physics, Korea University, Seoul, 136-701, Korea

M. Dobrowolska and J. K. Furdyna
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA
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CdSe quantum dots (QDs) in a ZnMnSe diluted magnetic semiconductor (DMS) matrix were investigated using both energy- and polarization-selective magneto-photoluminescence (PL). The peaks from Mn^{2+} internal transition, CdSe QDs, and ZnMnSe barrier were observed in the experiment done using above-barrier excitation. By examining the dependence of the PL peak intensity on magnetic field we were able to identify the competition between the Auger-type energy transfer process (i.e., the energy transfer from band electrons to Mn^{2+} ions) and energy relaxation into CdSe QDs in this QD system. The role of energy transfer processes between band electrons and Mn^{2+} ions in the DMS QDs was further studied by using excitation energy below the ZnMnSe band gap, where no change in the intensity of internal Mn^{2+} transitions with magnetic field was observed, indicating that the energy transfer from carriers excited into the ZnMnSe barrier is indeed responsible for the intensity behavior of these internal Mn^{2+} transitions observed in DMS QD structures.

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Spin-dependent phenomena in semiconductor quantum dot (QD) structures continue to be of interest to the scientific community because of the promise they hold for spintronic applications, e.g., as *q*-bits for quantum computation.[1] Since many spin properties are significantly enhanced in magnetic semiconductors, it is desirable to fabricate QD structure involving magnetic semiconductors in order to make use of that enhancement in zero-dimensional geometries. Specially, QD system containing one or a few Mn^{2+} ions would be very interesting in the view of manipulation and application of spin states.[2] II-VI-based QD systems have the advantage in this context, because they can act as very effective hosts for magnetic ions (such as Mn^{2+}), thus forming diluted magnetic semiconductors (DMS) systems.[3]

Magnetic semiconductor QD systems based on the CdSe/ZnSe combination have been successfully fabricated by introducing Mn^{2+} ions either into the quantum dots themselves, or into their surrounding matrix.[4–7] A very interesting phenomenon is commonly observed in these QD systems, the photoluminescence (PL) emission from the QDs is very weak at zero magnetic field (about two or three orders of magnitude weaker than that observed in the nonmagnetic CdSe/ZnSe QD system),[8] but is seen to increase quite dramatically when a magnetic field is applied.

Even though such intensity behavior of DMS QD systems is now well known, the physics behind this ubiquitous phenomenon is still under discussion. There are two suggested mechanisms for the effect. One proposed explanation suggests that the magnetic shrinkage of the exciton wave function suppresses the nonradiative recombination of the exciton in DMS QDs.[7] The other points to the energy transfer of excited carriers to Mn^{2+} ions—similar to the explanation used to describe the magnetic-field dependence of PL intensity in bulk ZnMnSe crystals.[9] Although the latter mechanism seems to be more generally accepted, it is important to bear in mind that the DMS QD system has two carrier capture centers—QDs and Mn^{2+} ions—and the competition between these two centers should be considered when one tries to understand the entire PL intensity behavior of DMS QD systems. In this paper we address the phenomenon of carrier relaxation in DMS QD system by systematic experiments using energy- and polarization-selective magneto-PL.

The CdSe QD samples were prepared by molecular beam epitaxy (MBE) using a Riber 32 R&D MBE machine equipped with elemental sources of Zn, Cd, Mn, and Se. A $Zn_{1-x}Mn_xSe$ buffer ($x \approx 0.15$) was first grown at 300 °C on (100) GaAs substrates to a thickness of approximately 1 μm. The QDs were formed by depositing 1.5 monolayers (MLs) of CdSe on the ZnMnSe buffer layer. After a 2 second break in the Se atmosphere the CdSe QDs were capped with ZnMnSe of the same Mn concentration as the buffer. Even though QDs are formed with nonmagnetic CdSe, diffusion of Mn^{2+} ions into CdSe QDs is inevitable since the QDs directly interfaced with ZnMnSe layers (i.e., with buffer and cap layers). The effect of Mn^{2+} diffusion into CdSe QDs will be discussed in the latter part of this paper, where the behavior of PL energy shift in the magnetic field is analyzed. The magneto-PL measurements were carried out in a variable temperature optical cryostat ($T \geqslant 1.5$ K) equipped with a 6 T superconducting magnet in the Faraday configuration. For the excitation of carriers, we have used either the 351 nm (3.53 eV) line of an Ar-ion laser (i.e., a photon energy above the ZnMnSe band gap), so that carriers were excited both from the QDs and from the ZnMnSe barriers or 458 nm (2.707 eV) line (i.e., a photon energy below the ZnSe band gap), so that only carriers inside the QDs are excited. For the polarization-selective measurements we used the combination of a quarter-wave plate and a linear polarizer in the detection. The PL signal was then analyzed by a SPEX spectrometer equipped with a liquid-nitrogen-cooled charge-

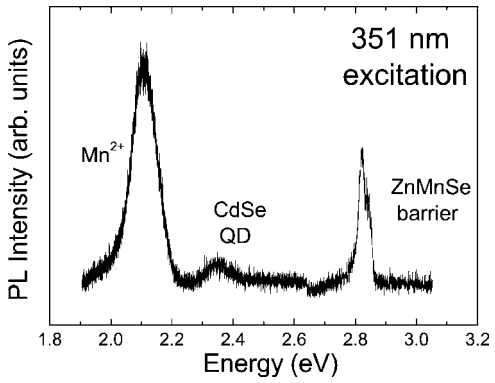

FIG. 1. PL spectrum taken at zero magnetic field on a CdSe/ZnMnSe QD system. The PL peaks from the internal Mn^{2+} transitions, from CdSe QDs and from the ZnMnSe barrier are clearly resolved.

coupled device (CCD) multichannel detector.

Figure 1 shows a typical PL spectrum of the QD structure obtained with excitation energy above the ZnMnSe band gap at zero magnetic field. The peaks from the internal Mn^{2+} transitions, the CdSe QDs, and the ZnMnSe barriers are seen at 2.1 eV, 2.35 eV, and 2.8 eV, respectively. It is conspicuous in the spectrum that, while the intensity of Mn^{2+} transition appears very strong, the CdSe QD peak is relatively weak. Such intensity quenching of the QD emission is rather unexpected, since QDs are known to be very efficient carrier capture centers, as has been experimentally demonstrated in CdSe/ZnSe QD systems by observing an order of magnitude stronger PL with above-ZnSe-band-gap excitation as compared to excitation below the band gap.[10] This suggests the existence of an energy transfer channel specific to carriers excited in the ZnMnSe barriers.

To further study the energy transfer processes in our QD system, we performed magneto-PL measurements with polarization-selective detection (i.e., the PL signal is detected with either σ^+ or with σ^- polarization). Such polarization-selective PL spectra observed on our QD systems exhibit significant changes in the emitted peak intensities when a magnetic field is applied. The magnetic field dependences of the peak intensities for the three observed peaks in above-barrier-excitation experiments are summarized in Fig. 2, where open and solid symbols represent the results obtained with σ^+ and σ^- polarizations, respectively. It is an interesting feature of the data that the PL intensities from both the CdSe QDs and the ZnMnSe barriers shows similar behavior (i.e., significantly increased intensities for the σ^+ polarization, and an intensity decrease for the σ^- polarization, typical for DMS systems), while the signal from the internal Mn^{2+} transitions monotonically decreases with increasing magnetic field independent of the polarization.

To understand the intensity phenomena of our DMS QD system, we adapted the model developed in Ref. 11, where an Auger-type energy transfer process between band electrons and Mn^{2+} ions was used to explain the photoconductivity behavior observed in CdMnS crystals. It is relatively simple to understand this phenomenon for a bulk crystal, since only one energy relaxation channel (i.e., between the band carrier and Mn^{2+} ions) is involved. The existence of

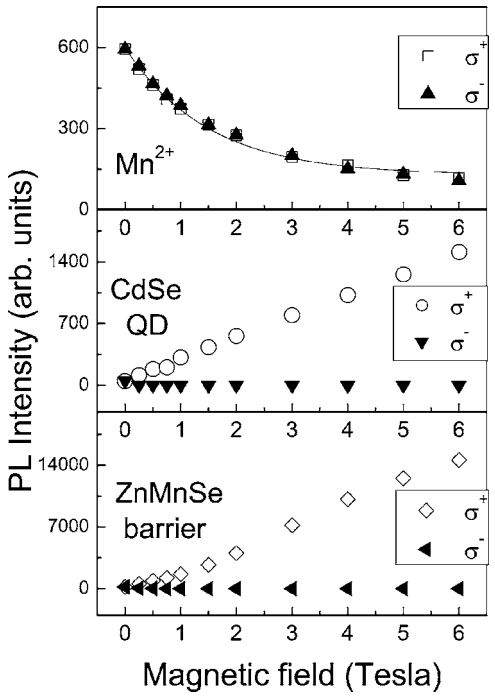

FIG. 2. Intensity variation as a function of magnetic field of the three types of PL peaks shown in Fig. 1. The open and solid symbols correspond to the data obtained with σ^+ and σ^- polarizations, respectively. While CdSe QD and ZnMnSe barrier peaks shows typical DMS characteristics (i.e., a significant increase for the σ^+ polarization, but a decrease for σ^-), the internal Mn^{2+} transition shows a monotonic decrease of intensity with increasing magnetic field for *both* polarizations. The solid line in the top panel is the calculated fit obtained using Eq. (1).

QDs in our system makes the energy relaxation mechanism somewhat more complicated, since now the QDs act as additional carrier capture centers. In the present case we must therefore consider two energy relaxation channels, direct transfer of excited carriers to Mn^{2+} ions (channel 1); and carrier transfer to CdSe QDs (channel 2), as schematically shown in Fig. 3. At zero magnetic field (see left-hand panel of Fig. 3), the energy transfer through channel 1 is much more efficient than through channel 2 for carriers excited in the ZnMnSe barrier because (a) the Mn^{2+} ions have a lower transition energy than the CdSe QDs; and (b) because the Mn^{2+} ions spatially overlap with the wave function of the excited carriers in ZnMnSe (i.e., Mn^{2+} ions exist in the ZnMnSe barrier). Therefore, even in a QD structure such as that used here the energy transfer to Mn^{2+} ions is the dominant process, thus resulting in stronger internal Mn^{2+} transitions than the PL from the CdSe QDs embedded in the ZnMnSe barriers. The similar phenomena can be expected from the ZnSe/ZnMnSe quantum well (QW) structures since the systems provide similar energy relation shown in Fig. 3. The magneto-PL study done on such QW structure indeed show significant enhancement of PL intensity from ZnSe QW,[12] implying existence of the energy transfer mechanism between the Mn^{2+} ions and carriers. Unfortunately, all previous study done on ZnSe/ZnMnSe QW structures did not investigate Mn^{2+} internal transition so that direct comparison to

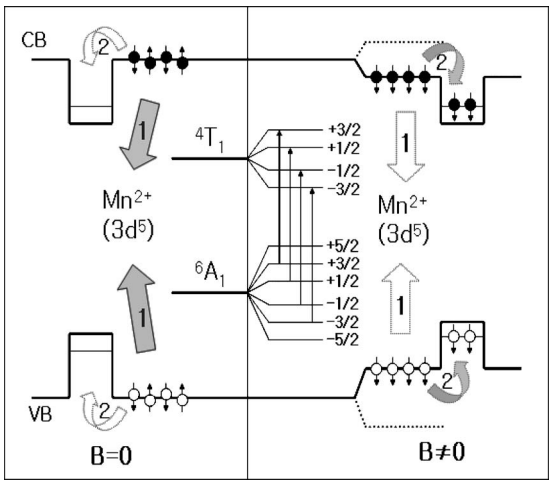

FIG. 3. Schematic diagram representing possible recombination processes. In the absence of a magnetic field (left panel), direct energy transfer to Mn^{2+} ions (channel 1) is stronger than carrier transfer to CdSe QDs, with subsequent relaxation via exciton recombination within the QDs (channel 2). In a magnetic field, channel 1 is suppressed due to spin polarization of excited carriers in the ZnMnSe barriers, and carrier relaxation via channel 2 becomes more effective as the field increases.

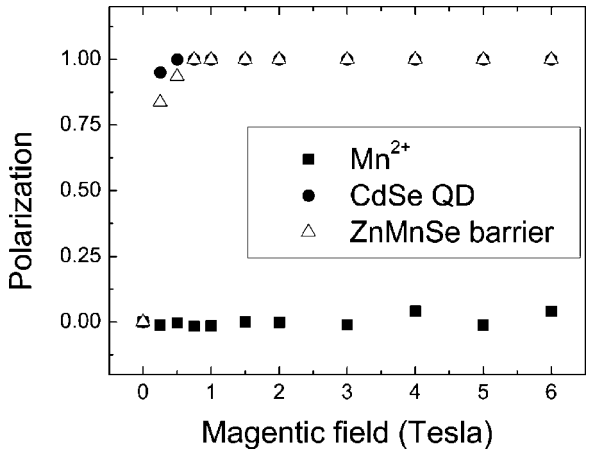

FIG. 4. Degree of polarization for internal Mn^{2+} transitions, transitions in CdSe QDs, and PL peaks corresponding to the ZnMnSe barriers. While the internal Mn^{2+} transitions show zero polarization in the entire magnetic field range, the QD and ZnMnSe barrier peaks are almost 100% polarized in the magnetic field region above about 0.5 T. Note that above this field the QD and ZnMnSe data points are indistinguishable.

our observation in QD structure is not available at the moment.

The situation changes significantly, however, when a magnetic field is applied. Recall that the (Auger-type) energy transfer process to the Mn^{2+} ions involves deexcitation of the photocreated conduction electron to the valence band, with simultaneous excitation of the Mn^{2+} ion from the $^6A_1$ ($S=5/2$) ground state to the $^4T_{1(2)}$ excited state with $S=3/2$. Since the process involves spin states, it is clearly sensitive to the spin arrangement of the electrons participating in it. The energy transfer through this process is allowed if the total spin projection before and after the process is conserved. The spin-dependent selection rule for single-ion-assisted Auger-type transitions is given by the following condition:

$$\mu + \sigma = \mu' + \sigma', \tag{1}$$

where σ and σ' are the spin projection for the conduction and valence electrons, respectively; and μ and μ' are, respectively, Mn^{2+} spin projections for the $S=5/2$ and $S=3/2$ states. In the absence of a magnetic field there are 16 equally probable combinations of electron spin and Mn^{2+} spin projections that satisfy this condition.

Since the transition selection rule is directly dependent on spin projection for the conduction and the valence electrons, the process will be significantly affected by an external magnetic field. When the field is applied, the band electron states of ZnMnSe undergo a giant spin splitting, characteristic of DMSs,[2] and consequently the band electrons become strongly spin polarized to one spin state. Such strong polarization of excited carriers is indeed observed in our QD system, as shown in Fig. 4, where the degree of polarization for transitions from ZnMnSe barriers, CdSe QDs, and Mn^{2+} ions are plotted as a function of magnetic field. It is clear that the PL peak from ZnMnSe is almost 100% polarized above a magnetic field of 0.5 T, indicating that the photoexcited electrons are completely spin-polarized within the time scale of exciton recombination time.[13] Once the band electrons are completely polarized, most of the spin combinations which were allowed at zero magnetic field become improbable, leaving in fact only four possible combinations, as shown in the right-hand panel of Fig. 3. One should note that the spin projection for $^6A_1$ ($S=5/2$) and $^4T_{1(2)}$ states involving those four possible combinations have the same values. This is because in the magnetic field the spin projections of band electrons have the same value in both the conduction and the valence band (i.e., both $\mu=-1/2$ and $\mu'=-1/2$), and the spin selection rules given in Eq. (1) then force the spin projection of the $^6A_1$ ($S=5/2$) and $^4T_{1(2)}$ spin sublevels of Mn^{2+} ions to also be the same. Thus transitions between internal states of Mn^{2+} involve no change in the spin projection, making the intensity behavior of these transitions polarization insensitive, as is clearly seen in the top panel of Fig. 2. Furthermore, the reduction of possible spin combinations for transitions through the recombination channel 1 makes energy transfer to Mn^{2+} ions less likely, thus causing the decrease in the internal Mn^{2+} transition intensity as the applied magnetic field increases.

When the magnetic field further increases and becomes sufficient to polarize the Mn spins, the transition probability for those four combination decreases exponentially as $\exp(-g_{\mathrm{Mn}}\mu_B B/k_B T)$, where μ_B is the Bohr mangeton, g_{Mn} is the Lande g-factor for Mn^{2+}, k_B is the Boltzmann constant, and T is the temperature at which the experiments are performed (i.e., 2 K). Since the intensity of the internal Mn^{2+} transitions is proportional to the transition probability for energy transfer described above, one may attempt to fit the intensity behavior of the internal Mn^{2+} transitions in the magnetic field using an exponential expression

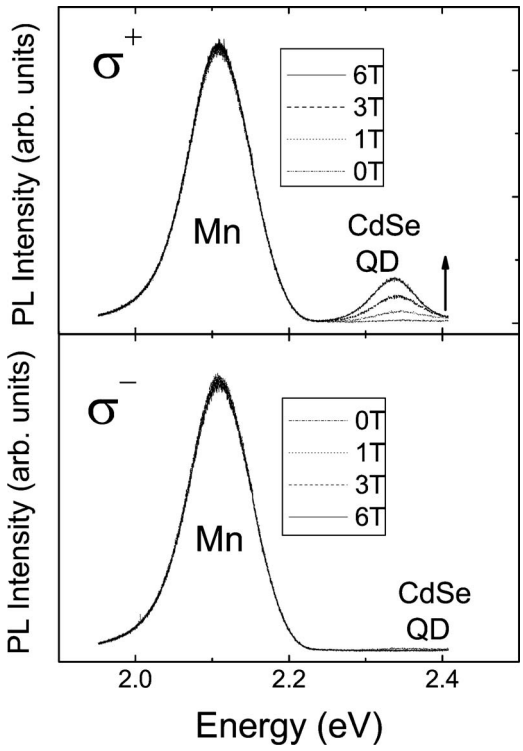

FIG. 5. PL spectra of CdSe/ZnMnSe QD system taken at various magnetic fields using excitation energy below the ZnMnSe band gap. The upper and lower panels represent the σ^+ and σ^- polarizations, respectively. The PL intensity from the CdSe QDs shows a strong dependence on the magnetic field and on polarization. In contrast, the internal Mn^{2+} transitions show almost no change with either magnetic field or polarization.

$$I(B) = \alpha + \beta \exp(-g_{\mathrm{Mn}}\mu_B B/k_B T). \quad (2)$$

Here α is a constant representing all contribution from field independent processes such as direct excitation of the Mn^{2+} ions by the laser and Auger-type transfer via Mn^{2+} ion pairs, and β represents the transition intensity at a certain magnetic field at which the carriers excited in the ZnMnSe barrier are completely polarized. The best fitting result was obtained with $\alpha=129$ and $\beta=471$, and is plotted as a solid line in the top panel of Fig. 2. The excellent fit to the experimental data strongly suggests that the model for the carrier energy transfer in the presence of a magnetic field as described above is indeed responsible for the intensity behavior of the observed internal Mn^{2+} transitions.

Once the carrier energy transfer through channel 1 is suppressed by the magnetic field as discussed above, the carrier relaxation via channel 2 becomes increasingly more effective, thus supplying more carriers into the CdSe QDs. Consequently, the PL intensity of CdSe QDs increases with increasing magnetic field. To further investigate the competition between the two carrier relaxation channels and its effect on the PL transition intensity observed in our DMS QD system, we performed additional magneto-PL experiments using excitation energy below the ZnMnSe band gap, so that no carriers are now supplied from the ZnMnSe barriers. The spectra obtained at several magnetic fields for two

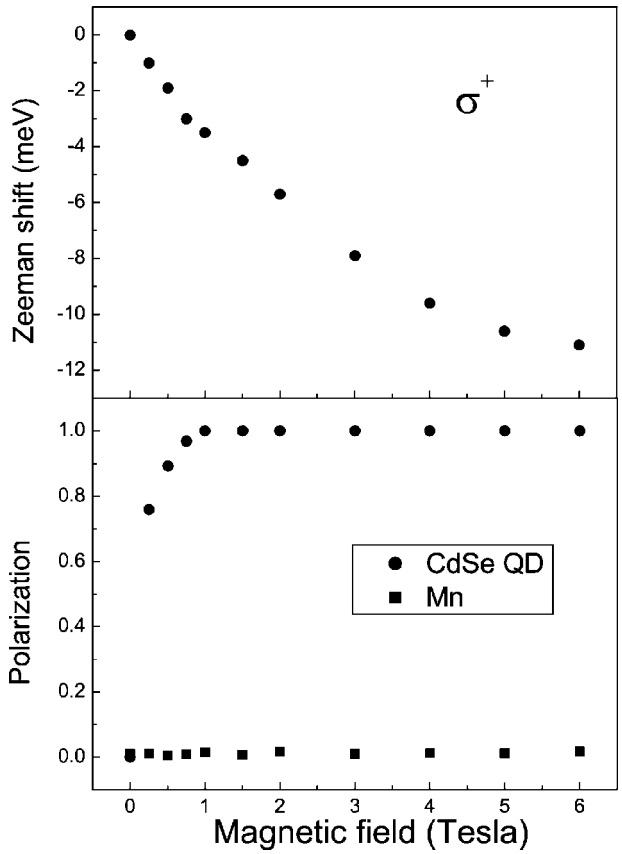

FIG. 6. Zeeman shift of CdSe QD emission obtained for the σ^+ polarization (upper panel); and the degree of polarization for the internal Mn^{2+} transitions and for CdSe QDs (lower panel). The observation of a large Zeeman shift indicates a finite carrier wave function overlap with Mn^{2+} ions. The vanishing degree of polarization of the internal Mn^{2+} transitions and the nearly complete polarization of the CdSe QDs peak in the high magnetic field region is similar to that observed in experiments done with excitation energy exceeding the ZnMnSe band gap (see Fig. 4).

opposite circular polarizations are shown in Fig. 5, where the Mn^{2+} internal transition and CdSe QD peaks are clearly visible. Since no carriers are excited in the ZnMnSe barrier, the energy transfer through channel 1 is now completely absent. The signal associated with the internal Mn^{2+} transitions observed in this experiment is therefore mainly from direct excitation of the Mn^{2+} states by the laser beam. The directly excited Mn^{2+} transition will not be influenced by magnetic field, since the spin polarized band electrons are not involved in this case. As seen in Fig. 5, the intensity of the observed internal Mn^{2+} transitions is indeed seen to be nearly insensitive to the magnetic field, in sharp contrast with the case of above-barrier excitation, where the intensity was observed to drop exponentially with increasing field. This clearly indicates that the carrier energy transfer through channel 1 determines the intensity behavior of the internal Mn^{2+} transitions when the carriers are produced in the ZnMnSe barrier.

It is interesting to notice that the PL from CdSe QDs shows a similar magnetic field dependence (i.e., an increase for the σ^+ polarization, and a decrease for the σ^- polarization), as observed in experiments involving above-barrier ex-

citation. In Fig. 6 we summarize the Zeeman energy shift and the degree of circular polarization of the PL emitted from the CdSe QDs. The observation of about 10 meV Zeeman shift, which is an order of magnitude larger that that of CdSe/ZnSe QDs, clearly indicates that the carriers inside the CdSe QDs experience the *sp-d* exchange interaction with Mn^{2+} ions. This interaction occurs because of finite wave function overlap of the QD excitons with Mn^{2+} ions in the ZnMnSe barrier, and/or with Mn^{2+} ions diffused into the CdSe QDs. The effects of carrier wave function overlap with Mn^{2+} ions have been observed in many quantum structures involving DMSs, and have been used as a tool for pinpointing the degree of carrier localization in those quantum structures.[14] Since our CdSe/ZnMnSe QDs are formed by depositing a very thin (i.e., 1.5 ML) layer of CdSe, the degree of both wave function penetration into the barrier and of diffusion of Mn^{2+} ions into the CdSe QDs are expected to be significant. Therefore, even though the carriers are excited only inside the CdSe QDs, they show characteristics that are qualitatively similar to those of carriers in DMS materials.

We note finally that one may find the polarization-insensitive behavior shown by the internal Mn^{2+} transitions somewhat surprising (see Figs. 3 and 6), since a polarization-dependent intensity variation of these transitions has been previously reported for experiments carried out on ZnMnSe crystals with polarization-selective excitation.[9] It should be noted, however, that—in contrast to those experiments, where an uneven population of spin carriers is produced by polarization-selective excitation—in the present study we use unpolarized light to excite the carriers, so that both spin states are equally populated. As already argued, and as shown schematically in Fig. 3, for the allowed internal Mn^{2+} transitions there is no change of the angular momentum or spin projection between the initial and the final states. Thus in our experiment the PL emission from internal Mn^{2+} transitions does not show any degree of circular polarization (i.e., a finite degree of circular polarization of the PL would require an angular momentum difference $\Delta m = \pm 1$ between initial and final states). This observation further supports the energy transfer model shown in Fig. 3 for the intensity behavior observed in this experiment.

In summary, we have systematically characterized the three types of optical transition which determine the PL spectra of the CdSe/ZnMnSe QD system recombination transitions within the QDs, direct recombination in the barrier, and internal Mn^{2+} transitions, including the interplay between these transitions. For above-barrier excitation, the observed exponential decay of the internal Mn^{2+} transition intensity in magnetic field is described very well by the energy transfer mechanism between excited carriers and Mn^{2+} ions. The observed insensitivity of the internal Mn^{2+} transitions to polarization throughout our entire magnetic field range further supports the energy transfer model proposed in this study. When the energy transfer to Mn^{2+} ions (referred to as channel 1 in this paper) is suppressed by an applied magnetic field, carrier transfer through direct recombination within the CdSe QDs (channel 2) becomes more effective, thus increasing the PL intensity associated with the QDs. These observations clearly demonstrated that there exists a competition between the two parallel energy relaxation channels in our DMS QD system.

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*Electronic address: slee3@korea.ac.kr

[1] D. Loss and D. P. DiVincenzo, Phys. Rev. A **57**, 120 (1998).
[2] L. Besombes, Y. Léger, L. Maingault, D. Ferrand, H. Mariette, and J. Cibert, Phys. Rev. Lett. **93**, 207403 (2004).
[3] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).
[4] C. S. Kim, M. Kim, S. Lee, J. Kossut, J. K. Furdyna, and M. Dobrowolska, J. Cryst. Growth **214/215**, 395 (2000).
[5] P. R. Kratzert, J. Puls, M. Rabe, and F. Hennenberger, Appl. Phys. Lett. **79**, 2814 (2002).
[6] G. Bacher, H. Schömig, M. K. Welsch, S. Zaitsev, V. D. Kulakovskii, A. Forchel, S. Lee, M. Dobrowolska, J. K. Furdyna, B. König, and W. Ossau, Appl. Phys. Lett. **79**, 524 (2001).
[7] K. Shibata, K. Takabayashi, I. Souma, J. Shen, K. Yanata, and Y. Oka, Physica E (Amsterdam) **10**, 358 (2001).
[8] S. Lee, L. V. Titova, M. Kutrowski, M. Dobrowolska, and J. K. Furdyna, J. Korean Phys. Soc. **42**, S531 (2003).
[9] V. G. Abramishvili, A. V. Komarov, S. M. Ryabchenko, and Yu. G. Semenov, Solid State Commun. **78**, 1069 (1991).
[10] J. K. Furdyna, S. Lee, A.-L. Barabasi, and J. L. Merz, in *II-VI Semiconductor Materials and Their Applications*, edited by M. C. Tamargo (Taylor and Francis, 2001), pp. 313–354.
[11] M. Nawrocki, Yu. G. Rubo, J. P. Lascaray, and D. Coquillat, Phys. Rev. B **52**, R2241 (1995).
[12] V. V. Rossin, J. Puls, and F. Henneberger, Phys. Rev. B **51**, R11209 (1995).
[13] The exciton recombination time is in the range of a few nanosecond; and the spin-flip time of carriers in DMSs is in the range of picoseconds. Therefore, carriers are almost completely spin polarized before their recombination.
[14] S. Lee, M. Dobrowolska, J. K. Furdyna, and L. R. Ram-Mohan, Phys. Rev. B **59**, 10302 (1999).