Femtosecond spin spectroscopy in magnetically tunable heterostructures

D. A. Tulchinsky, J. J. Baumberg, and D. D. Awschalom
Department of Physics, University of California, Santa Barbara, California 93106

N. Samarth
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

H. Luo and J. K. Furdyna
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556
(Received 14 March 1994; revised manuscript received 7 June 1994)

Spin-flip scattering of oriented carriers between Zeeman-split quantum-confined states is observed directly by femtosecond-resolved photoluminescence spectroscopy in magnetically coupled double quantum wells. Polarization measurements reveal that the spin dynamics are determined by the initial carrier energy *and* spin orientation with respect to the Zeeman separation of the levels. Studies as a function of applied field and barrier thickness show that spin equilibration is remarkably sensitive to the magnetic environment.

The dynamics of interacting carriers in quantum-confined heterostructures continues to be an area of considerable experimental and theoretical interest, and has led to a deeper understanding of the energy-relaxation processes for excitons in semiconductor quantum wells.[1] However, there have been comparatively few investigations of *spin* dynamics in confined systems.[2–5] An attractive geometry for studying the role of quantum confinement in spin relaxation is a double-quantum-well (DQW) structure containing a diluted magnetic semiconductor (DMS) as the separating barrier. Upon application of a magnetic field, the presence of paramagnetic ions in the DMS barrier produces a spin-dependent coupling between the wells that is suitably tailored by the specific structure design. The giant Zeeman splitting of the barrier's band edges breaks the spin degeneracy[6] and modifies the tunneling potential [Fig. 1(a)]. Here we describe polarization-resolved photoluminescence measurements in which an initially polarized exciton population is subsequently monitored with femtosecond resolution. Systematic studies directly reveal spin-flip scattering between the two Zeeman-split spin states, whose energy separation is continuously tunable by the applied field. The spin-relaxation process is markedly dependent on the excitons' injection energy, spin orientation, and the Zeeman splitting of the final spin states. These measurements demonstrate the utility of spin spectroscopy in probing dynamical reorientation from magnetic layers of near-atomic thicknesses.

The experiments use a series of II-VI double quantum wells that are coupled by a thin DMS barrier as depicted schematically in Fig. 1(a). The samples are grown by molecular-beam epitaxy on (100) GaAs and consist of two nonmagnetic 40-Å-wide $Zn_{0.77}Cd_{0.23}Se$ quantum wells separated by a magnetic $Zn_{0.76}Mn_{0.24}Se$ barrier of thickness $L_B = 12$, 24, or 32 Å. The DQW structure is coherently strained between a 6000-Å buffer layer and a 2000-Å cap layer of ZnSe. A nonmagnetic sample with a 12-Å-thick ZnSe barrier is used as a control. Static photoluminescence (PL) measurements are used to establish the structure quality and to evaluate their basic magneto-optical properties.[7] The samples are positioned in a variable-temperature magneto-optical cryostat ($B = 0-5$ T) in the Faraday configuration. Circularly polarized light with incident power < 1 mW photoexcites $\sim 10^{10}$-cm^{-2} carriers in the symmetric $n = 1$ quantum-well state. Absorption studies show[8] that the luminescence spectra arise from exciton recombination from the $n = 1$ conduction-band ground state to the $n = 1$ heavy-hole ground state. Symmetry considerations show that under application of a magnetic field B_Z, two Zeeman-split spin states $S_Z = \pm 1$ absorb (or emit) either left [$\sigma -$] or right [$\sigma +$] circularly polarized light corresponding to excitation (luminescence) of spin-up or spin-down electron-hole pairs, respectively [Figs. 1(a) and 1(b)]. Independent excitation and resolution of the two spin states is achieved by appropriately combining a $\lambda/4$ plate and linear polarizer to both produce and analyze the desired circular polarization. This technique allows us to independently monitor the evolution of each spin state under a variety of conditions. By selectively exciting excitons of one spin state, we can track the evolution of that exciton's spin orientation by monitoring its time-dependent luminescence. Furthermore, carrier spin flip is directly observed by measuring the onset of luminescence from those carriers which spin scatter into the opposite spin orientation.

Time-resolved photoluminescence spectroscopy is performed using the sum-frequency upconversion technique.[9–11] In this method, a laser pulse excites the sample, while a time-delayed probe pulse interrogates a time slice of the collected luminescence as the two pass coincidentally through a nonlinear crystal. Sum-frequency photons are generated for those luminescence and probe photons which satisfy the phase matching conditions of the crystal. In practice, 100-fs excitation pulses between

0163-1829/94/50(15)/10851(5)/$06.00

2.480 and 2.755 eV with a full width at half maximum (FWHM) of 15 meV are generated by collinear second-harmonic generation in a thin β-barium borate (β-BBO) nonlinear crystal using the nearly transform-limited infrared output of a mode-locked Ti:sapphire laser. Sum-frequency photons are generated efficiently by mixing a portion of the infrared laser with the collected luminescence in a second β-BBO crystal, resulting in time resolution of $\Delta t \sim 150$ fs. After mixing, the sum-frequency photons are collected and resolved by a monochrometer with 10-meV resolution tuned to the peak energy of the exciton luminescence, and then detected by a cooled photomultiplier tube.[3]

The energy position of the Zeeman-split spin states is determined by static PL data. Figure 1(b) shows an example for a structure having a barrier width $L_B = 12$ Å in $B = 4$ T. At $T = 4.6$ K the field-induced separation of the two spin states is centered about the $E = 2.525$ eV, zero-field luminescence peak with an energy splitting $\Delta E = 12.8$ meV which corresponds to a g factor of ~ 55. The difference in the peak intensities yields a net polarization $P = [I\downarrow - I\uparrow]/[I\downarrow + I\uparrow] = 0.80$.[7] As seen in Fig. 1(b), the excitation energy is tuned to a value above the zero-field ground state, with the excess energy denoted by Δ. The 15 meV FWHM bandwidth of the laser results from the nearly transform-limited laser pulse. In contrast to spin scattering dynamics, the time-resolved PL intensity gives the exciton *lifetimes* as shown in Fig. 1(c). The data are taken at the energy of the static luminescence peak for each field and spin orientation, respectively. In this particular case the excitons are excited with linearly polarized light to prepare equal spin populations and ensure that spin reorientation does not significantly modify the measured recombination lifetime. The lifetimes for both spin states are calculated using a least-squares fit to a single decaying exponential, and are seen to be nearly identical for both orientations. The times range from $\tau = 56.3 \pm 1.1$ ps at $B = 0$ T to $\tau = 36.9 \pm 1.2$ ps at $B = 4$ T, slowly decreasing with increasing magnetic field.

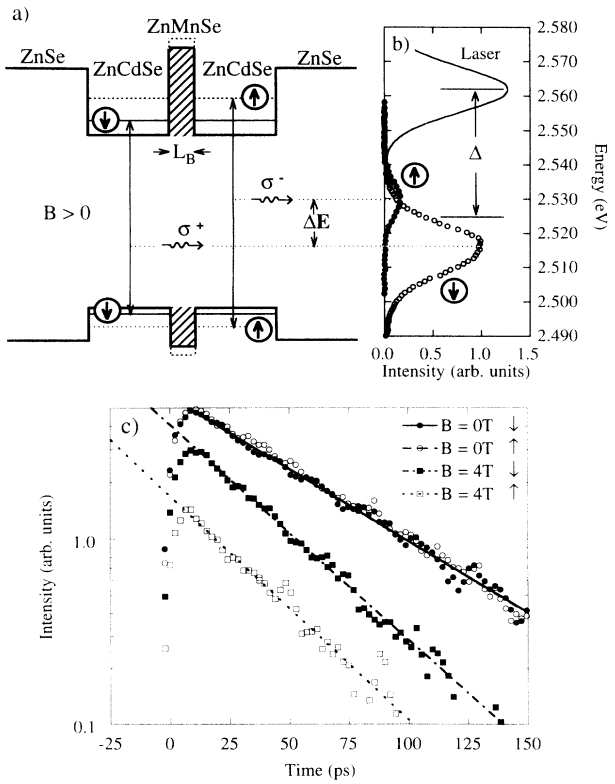

FIG. 1. (a) Schematic diagram of the band alignment of a $ZnSe/Zn_{1-x}Cd_xSe/Zn_{1-y}Mn_ySe$ DMS coupled double quantum well. (b) Polarization-resolved static PL spectra from a structure consisting of two 40-Å-wide $Zn_{0.77}Cd_{0.23}Se$ wells coupled by a $L_B = 12$ Å $Zn_{0.76}Mn_{0.24}Se$ DMS barrier at $T = 4.6$ K in $B = 4$ T. Solid (open) circles represent PL from spin-up (-down) radiating excitons. The Zeeman energy splitting of the peaks is $\Delta E = 12.8$ meV. The energy difference between the excitation energy and the zero-field ground state is given by Δ. (c) Time-resolved PL from exciton recombination in two fields for each polarization. The lines are least-squares fits to the data to extract the carrier lifetimes.

Time-resolved polarization spectroscopy is used to probe the spin dynamics of the quantum-confined carriers as a function of their initial orientation and energy. The time-resolved photoluminescence intensity dynamically reflects the band-edge carrier population, as shown in Figs. 2(a) and 2(b) for the sample with a barrier of width $L_B = 12$ Å at $T = 4.6$ K in $B = 4$ T. Oriented excitons are excited by circularly polarized light at 2.530 eV, 5 meV in excess of the ground state. These two figures differ only in the orientation of the initial exciton spins, either spin-down [Fig. 2(a)] or spin-up [Fig. 2(b)]. In each case the luminescence is polarization analyzed ($I\downarrow, I\uparrow$) to reveal the final spin orientation of the radiating carriers. In $B = 4$ T, the 12.8-meV Zeeman splitting of the barrier potential causes the spin-down state to be energetically favorable. Thermodynamics predicts that the spin populations will attempt to equilibrate via entropy considerations but, as the energy gap ΔE increases between the two states, the populations become increasingly unbalanced. In contrast to spins prepared in the lower-energy spin-down state, carriers prepared in the high-energy spin-up state [Fig. 2(b)] rapidly spin flip and equilibrate the spin population within ~ 20 ps, after which there are marginally more carriers recombining from the opposite spin-down state. Note that this is not an artifact of spin-dependent recombination lifetimes, which would deplete one spin population faster than the other. The dynamic difference in the spin population is explicitly shown by the time-resolved carrier polarization. Figure 2(c) shows the dynamical polarizations for the two initial spin configurations. In contrast, Fig. 2(d) contains data for the comparable nonmagnetic control sample (ZnSe barrier) under similar conditions. The marked difference in their behavior demonstrates that spin relaxation of quantum-confined carriers is strongly modified by the presence of a few magnetic monolayers.

In order to investigate how the energy splitting ΔE between the two spin states influences the spin scattering, systematic studies of the polarization at several values of the applied magnetic field are shown in Fig. 3 for the $L_B = 12$ Å magnetic barrier sample. In the absence of a magnetic field, Fig. 3 shows that the spin scattering time

is approximately 10–20 ps for the degenerate states. While such times may be qualitatively determined from the decay of the polarization, specific scattering times are difficult to obtain since these processes do not follow a known functional relaxation. The evolution of the polarizations are identical, mirroring the initial carrier orientation and the equilibrating entropically towards zero polarization within time scales approaching the carrier lifetime. Applying a magnetic field removes the spin degeneracy, making the evolution of the polarization asymmetric with respect to the initial spin orientations. The spin-relaxation rate for spin-up injected carriers [Fig. 3(b)] is relatively unchanged by the magnetic field, with only the final equilibrium polarization being field dependent. However, as the Zeeman energy gap widens to 12.8 meV in $B=4$ T, spin-down injected carriers remain polarized [Fig. 3(a)]. The reorientation is suppressed to such an extent that recombination from carriers which have spin flipped is nearly undetectable in this field. Figure 3 clearly shows that the magnetically aligned ions in the barrier affect spin relaxation from the two spin states quite differently. This hypothesis is corroborated qualitatively by Faraday rotation experiments performed on these samples.[8] In those experiments, spin-down carriers are less likely to exchange angular momentum with the magnetic ions in the barrier due to the high-energy cost of counteraligning the magnetic ions with the external field. However, this is not the case for spin-up carriers, where angular-momentum exchange leads to a favorable realignment of magnetic moments with the external field. The same mechanisms are consistent with our observation that the spin-up carrier reorientation rate is unaffected by the field, while the spin-flip rate for spin-down carriers is suppressed.

Prior experimental measurements[3,12,13] and theoretical investigations[4,14,15] have suggested that spin relaxation in III-V and II-VI quantum systems might accompany energy/momentum relaxation via LO-phonon emission ($\hbar\omega_{LO}\sim 30$ meV here) resulting in spin scattering times of order ~ 10–20 ps. Figure 4 shows the spin relaxation for the $L_B=12$ Å sample at $T=4.6$ K, in an applied magnetic field of 2 T ($\Delta E=6.4$ meV) for several different excitation energies above the zero-field ground state at 2.525 eV. It is clear that the scattering dynamics are highly

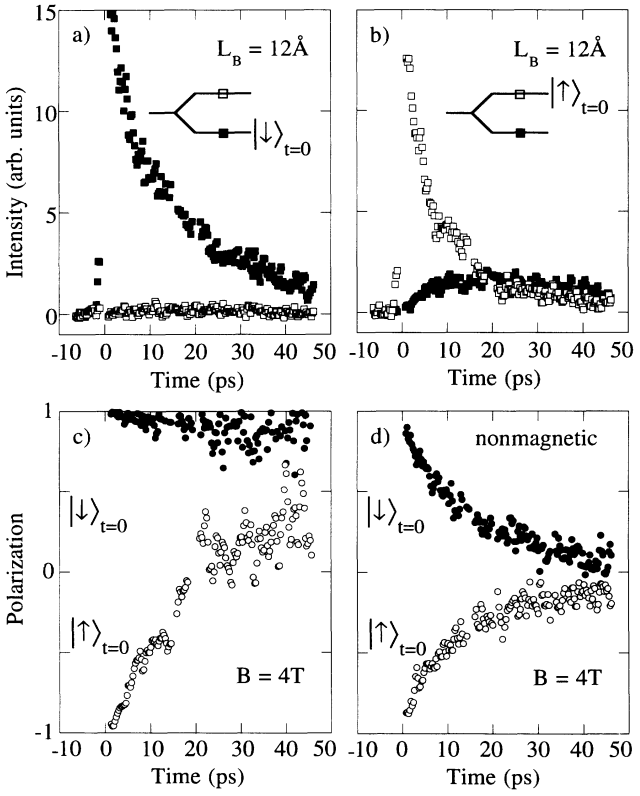

FIG. 2. Time- and spin-resolved PL from the sample of Fig. 1 at $T=4.6$ K in $B=4$ T for (a) carriers initially orientated spin-down, and (b) spin-up excited at 2.530 eV. In each case solid (open) symbols represent the energetically (un)favored spin-down (spin-up) component of the luminescence detected at 2.525 eV. (c) The resulting time-dependent polarization $P=[I\downarrow-I\uparrow]/[I\downarrow+I\uparrow]$, where solid (open) symbols represent the polarization from spin-down (spin-up) injected carriers. (d) Analogous measurements to (c) for a nonmagnetic control sample under similar conditions.

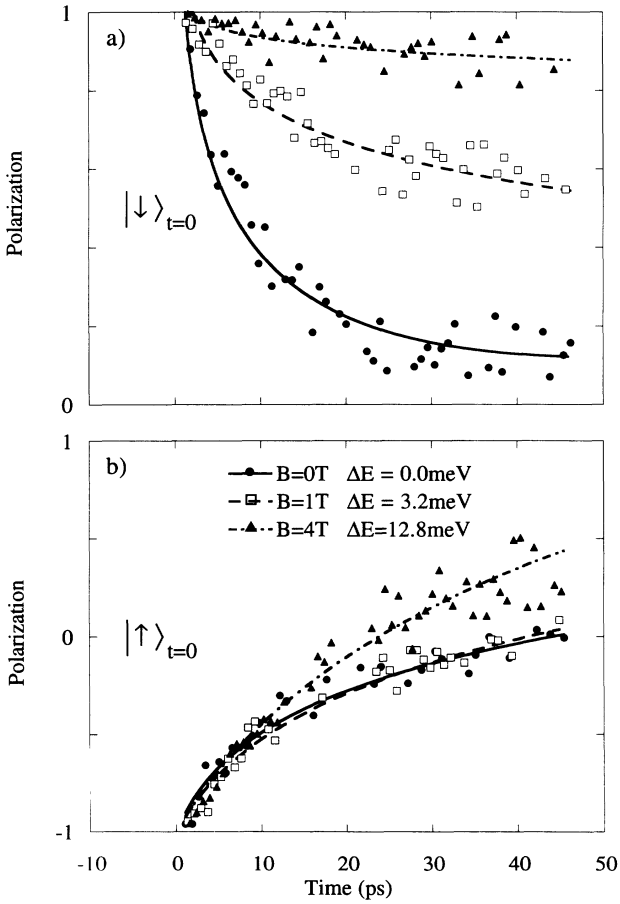

FIG. 3. Time-resolved polarization from the sample of Fig. 1 at $T=4.6$ K, excited 5 meV above the peak luminescence in increasing magnetic fields for carriers injected (a) spin-down, and (b) spin-up. Points have been removed for clarity and the lines serve as guides to the eye. The measured Zeeman splitting ΔE is given for each field.

dependent on the excess energy (Δ) of carriers injected into the quantum structure. In Fig. 4(a), where carriers are injected $\Delta \sim 5$ meV above the luminescence peak, it is seen that the initial polarization is $\sim 100\%$ for either pump orientation shortly after $t=0$, and carriers continue to spin relax with spin reorientation times longer than the carrier recombination lifetime. This is in sharp contrast to the case when carriers are excited with greater kinetic energies, and must first cool to the ground state by losing energy and momentum prior to recombination. Figure 4(d) shows the time-resolved polarization for carriers injected $\Delta \sim 100$ meV above the ground state. Despite being excited with spin-up photons, the initial time-resolved polarization indicates that the luminescing excitons are more spin-down polarized (within the ~ 200 fs time resolution of the experiment). Such a rapid reorientation of the injected spin-up state clearly suggests concurrent spin flip and energy relaxation of carriers, though the mechanism for this action is still unresolved. Figure 4(d) also indicates that the rate at which further band-edge spin scattering completes the spin relaxation and brings the two carrier populations to equilibrium is also increased by $\sim 80\%$. Furthermore, we observe extremely rapid spin scattering (<200 fs) when excitons are created with large excess energies. It is worth noting that this fast relaxation is also seen in the nonmagnetic control sample. This scattering is much faster than energy-relaxation processes and seems unusually fast for LO-phonon interactions. The subsequent band-edge spin scattering at later times, comparable with LO-phonon scattering rates, is modified by the magnetic field only in those samples containing a magnetic barrier.

To investigate the role of the magnetic barrier width on spin scattering, Figs. 5(a) and 5(b) show the time- and spin-resolved photoluminescence for two samples with different barrier thicknesses (12 and 32 Å, respectively) at $\Delta = 5$ meV. These data reveal that while the decay rate of the photoluminescence sample is unaffected by the field for a wide barrier, the rate of decay of the luminescence in the 12-Å barrier sample increases as a field is applied. This faster decay results in roughly comparable luminescence intensities by ~ 30 ps. The modified spin scattering

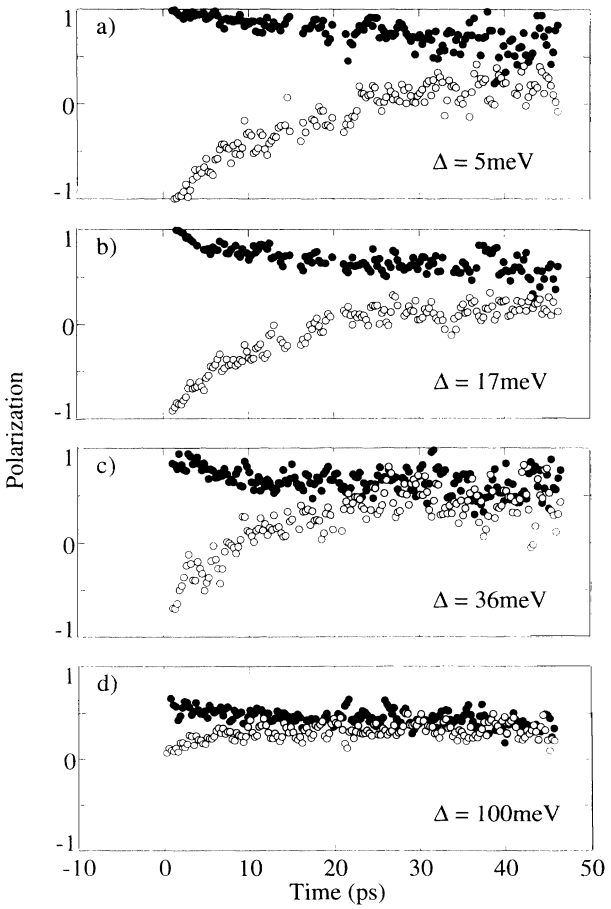

FIG. 4. Time-resolved polarization from the sample of Fig. 1 at $T=4.6$ K in a 2-T magnetic field for increasing excitation energy, Δ, in excess of the ground-state luminescence. Solid (open) symbols represent the polarization from spin-down (spin-up) injected carriers.

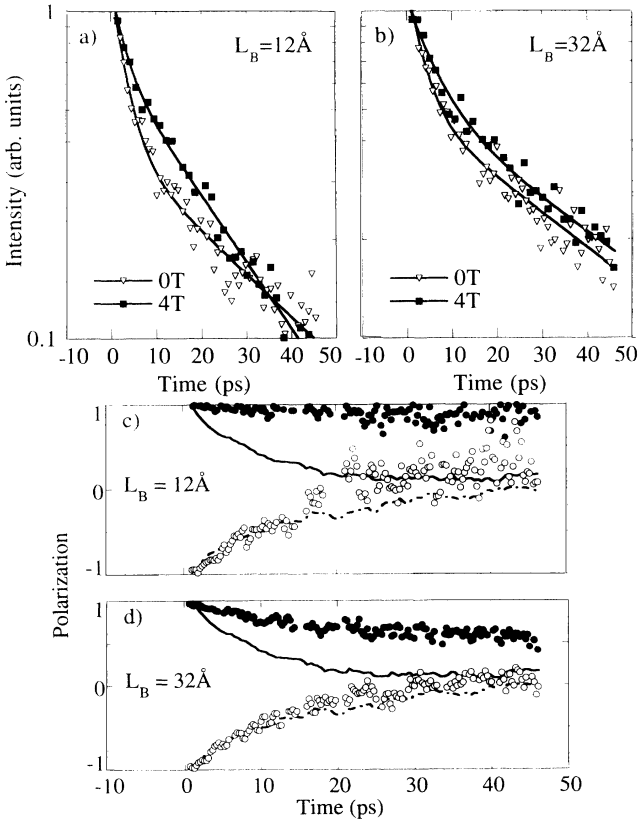

FIG. 5. Time- and spin-resolved PL at different values of the magnetic field for carriers both excited ($\Delta=5$ meV) and detected spin-down in a magnetically coupled DQW at $T=4.6$ K with barrier (a) $L_B=12$ Å and (b) $L_B=32$ Å. The curves are normalized by their magnitude at $t=0$. Solid lines serve as guides to the eye, and points have been removed for clarity. The resultant time-resolved polarization for the DQW with (c) $L_B=12$ Å and (d) $L_B=32$ Å. The solid (dashed) line shows the polarization from spin-down (spin-up) injected carriers at 0 T. Solid (open) symbols show the polarization from spin-down (spin-up) injected carriers at 4 T.

rates observed only in the 12-Å barrier sample indicate that enhanced field-induced alignment of ions in lower-dimensional barriers may play a role in the spin scattering process.[3,8] Furthermore, the decay of the polarization, as shown in Figs. 5(c) and 5(d), confirms that spin scattering rates are both field and orientation dependent. In the 32-Å barrier sample, the rate of spin reorientation for spin-up injected carriers is unaffected by the field and never achieves the degree of spin equilibration seen with spin-down injected carriers. Instead the dynamics matches those seen in zero external field. In the sample with the thinner barrier, however, both spin orientation decay rates are modified by the field with a more dramatic effect on injected spin-down carriers. Moreover, the difference in relaxation rates between the two samples is far greater than suggested by the differences in their magnetization[7] due to changes in dimensionality. The barrier width clearly affects the spin scattering rates in addition to modifying the final equilibrium polarization.

In summary we have measured spin-dependent dynamics of carriers in a magnetically coupled double quantum well using femtosecond polarization-resolved upconversion spectroscopy. Spin-selective relaxation of photoexcited carriers is directed by the breaking of spin degeneracy and magnetic control of the resulting scattering path. Utilization of conventional semiconductor heterostructures which incorporate magnetic spins opens additional avenues in which to explore spin interactions in magnetic quantum systems.

We thank J. W. Wilkins and J. C. Egues for critical readings of the manuscript. This work was supported in part by NSF Grant Nos. DMR 92-07567 and DMR 92-08400. D.A.T. acknowledges the support of AFOSR Grant No. F49620-93-1-0446.

[1]S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).
[2]M. R. Freeman, D. D. Awschalom, J. M. Hong, and L. L. Chang, Phys. Rev. Lett. **64**, 2430 (1990).
[3]J. F. Smyth, D. A. Tulchinsky, D. D. Awschalom, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. Lett. **71**, 601 (1993).
[4]T. Uenoyma and L. J. Sham, Phys. Rev. Lett. **64**, 3070 (1990).
[5]G. Bastard and L. L. Chang, Phys. Rev. B **41**, 7899 (1990).
[6]*Diluted Magnetic Semiconductors,* edited by J. K. Furdyna and J. Kossut (Academic, San Diego, 1988), Vol. 25.
[7]J. F. Smyth, D. D. Awschalom, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. B **46**, 4340 (1992).
[8]J. J. Baumberg, S. A. Crooker, D. D. Awschalom, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. B **50**, 7689 (1994).
[9]H. Mahr and M. D. Hirsch, Opt. Commun. **13**, 96 (1975).
[10]J. Shah, IEEE J. Quantum Electron. **24**, 276 (1988).
[11]M. R. Freeman and D. D. Awschalom, J. Appl. Phys. **67**, 5102 (1990).
[12]T. C. Damen, L. Vina, J. E. Cunningham, and J. Shah, Phys. Rev. Lett. **67**, 3432 (1991).
[13]H. Krenn, K. Kaltenegger, and G. Bauer, Solid State Electron. **31**, 481 (1988).
[14]*Optical Orientation,* edited by F. Meier and B. P. Zakharchenya (North-Holland, Amsterdam, 1984), Vol. 8.
[15]M. Z. Maille, E. A. de Andrada e Silva, and L. J. Sham, Phys. Rev. B **47**, 15 776 (1993).