Observation of long-lived exciton magnetic polarons in $Zn_{1-x}Mn_xSe/ZnSe$ multiple quantum wells

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(Received 18 July 1994)

Using time-resolved photoluminescence to study $Zn_{1-x}Mn_xSe/ZnSe$ multiple quantum wells, we show that the formation and decay kinetics of exciton magnetic polarons (EMP's) depend strongly upon the Mn concentration. We suggest that as the Mn ion concentration in the barrier is increased, three different types of EMP may form: (i) both the electron and hole are confined to the magnetic material (type-I EMP), (ii) the electron and hole are spatially separated (type-II EMP), or (iii) confined at the interface. In agreement with previous results in thick epilayers, we find that *both* the formation time and recombination lifetime of the type-I EMP are approximately 400 ps, so that the majority of the EMP's never fully achieve their equilibrium configuration. In contrast, the recombination lifetime of the spatially indirect type-II EMP observed here is greater than 20 ns (nearly forty times the formation time), so that the EMP's in quantun wells may be studied in thermal equilibrium.

The electronic structure of diluted magnetic semiconductors (such as the II-VI material $Zn_{1-x}Mn_xSe$) is strongly affected by the strong exchange interaction between the delocalized electrons (*s*-like) and holes (*p*-like) and the localized *d* electrons on the magnetic impurities. This (*sp-d*) exchange interaction is responsible for the spectacular magneto-optical phenomena observed in these materials: the giant Zeeman-like splitting of the conduction and valence bands,[1] large Faraday rotations,[2] and the formation of the bound magnetic polaron.[3-5] In addition, the large *sp-d* exchange coupling has been used to "engineer" spin heterostructures such as the recently discovered magnetically induced type-I/type-II transition observed in $Zn_{1-x}Fe_xSe/ZnSe$,[6] $Zn_{1-x}Mn_xSe/ZnSe$,[7] and $Cd_{1-x}Mn_xTe/CdTe$ (Refs. 8 and 9) heterostructures, and the formation of $Zn_{1-x}Fe_xSe/ZnSe$ (Refs. 10 and 11) and $Zn_{1-x}Mn_xSe/ZnSe$ (Refs. 11 and 12) spin superlattices. In these cases, the heterostructure band alignment in a magnetic field is determined by comparison of the Zeeman-like spin splitting of the conduction and valence bands with the intrinsic heterostructure band offsets. In the case of the spin superlattices, the magnetic-field effects are much larger than the band offsets so that the confinement of the electrons and holes are completely determined by their spin state. The spin-up electrons and holes are confined to the nonmagnetic layers, while the spin-down electrons and holes are confined to the magnetic layers. In contrast, the confinement of electrons in the type-II structures is determined by the intrinsic band offsets, while the hole confinement is determined by the magnetic interactions.

In this paper, we demonstrate that this relation between the exchange energy and band offset has important implications for the band alignments of magnetic polarons in two-dimensional structures. Magnetic polarons are formed when electrons or holes lower their energy through spontaneous magnetization of the local magnetic impurities. Because the spontaneous magnetization of the magnetic impurities is effectively equivalent to the application of an external field, considerations of the relative band alignments of the electrons and holes are equally important in this case as well. We propose that three different types of exciton magnetic polarons (EMP's) may form in these two-dimensional magnetic structures. Depending upon whether or not the strength of the magnetic interactions are sufficient to outweigh the intrinsic conduction- and valence-band offsets in these materials, the EMP's may have (i) both the electron and hole confined to the magnetic material (type-I EMP), (ii) the electron and hole spatially separated (type-II EMP), or (iii) confined at the interface. In what follows, time-resolved magnetophotoluminescence experiments in $Zn_{1-x}Mn_xSe/ZnSe$ heterostructures are presented that provide evidence for formation of *both* type-I and type-II EMP's, with the electrons and holes completely confined to the magnetic layers in the one case, and spatially separated with the electrons in the nonmagnetic wells and the holes in the magnetic barriers in the second case. In both cases, the EMP forms in less than a nanosecond, while the recombination lifetime of the spatially indirect EMP in the 14% multiple quantum well (MQW) is over 20 times longer—consistent with the large type-II electron-hole spatial separation.

While the magnetic polarons formed by donor-bound electrons, or bound excitons in bulk crystals, are well understood experimentally[3-5] and theoretically,[13,14] much less is known concerning the effects of dimensionality on the magnetic polarons. Several groups published magnetophotoluminescence data from $Cd_{1-x}Mn_xTe/CdTe$ quantum wells that indicated that the EMP's in these structures are confined at the interface between the magnetic and nonmagnetic layers.[15-19] However, the EMP's in these structures exhibit short recombination lifetimes of less than 500 ps that were comparable to the EMP's formation time, and that became shorter upon application of an external magnetic field.[20] This behavior is expected since the high alloy concentration (> 30%) in the $Cd_{1-x}Mn_xTe$ layers is sufficient to confine both the elec-

trons and holes through the intrinsic band offsets, regardless of field. In contrast, Awschalom *et al.*[21] measured the dynamic magnetization in type-II ZnTe/$Cd_{1-x}Mn_xSe$ quantum wells where the holes are strongly confined to the *nonmagnetic* ZnTe layers and the electrons are confined to the *magnetic* $Cd_{1-x}Mn_xSe$ layers by the intrinsic band offsets.[22] Surprisingly, even in this case where the electron and hole are spatially separated, the polaron lifetime was found to be relatively short and comparable to the polaron formation time.

In the experiments reported here, we have varied the Mn concentration in $Zn_{1-x}Mn_xSe/ZnSe$ multiple quantum wells from 2% to 14% in order to control the differences between the exchange energies and the band offsets. In particular, we will discuss results from three molecular-beam-epitaxy prepared $Zn_{1-x}Mn_xSe/ZnSe$ multiple quantum wells each with four periods of alternating 100-A ZnSe and $Zn_{1-x}Mn_xSe$ layers, but with different Mn concentrations of 2%, 4%, and 14%. Magnetoresistivity measurement of these samples showed that the 2% and 4% samples are spin superlattices at fields above 0.5 T, while the 14% MQW has a type-II alignment at fields above 0.5 T.[23]

The samples were mounted in a strain-free manner onto a copper block inside a Janis Super-Varitemp cryostat, where the temperature was monitored by a calibrated Si-diode temperature sensor and controlled by a computer. Photoexcitation was provided by a frequency-tripled mode-locked Nd:YAG (yttrium aluminum garnet) laser, which provided 80-ps pulses at a wavelength of 354.7 nm. The laser beam was focused to a 1-mm-diam spot onto the samples, and the average power density kept to less than 1 mW/cm^2 to avoid heating effects. The photons emitted from the samples were energy dispersed by a $\frac{3}{4}$-m SPEX single monochrometer and detected by a fast Hamamatsu Micro-Channel plate photomultiplier tube with a temporal dispersion of 40 ps. The standard time-correlated photon-counting techniques were used to obtain complete time-resolved spectra by using a computer to accumulate the time decays of the photoluminescence at every spectral point. The time response of the system was less than 80 ps.

Figure 1 shows a representative time-resolved photoluminescence (PL) spectrum of the 14% MQW at 2.8 K in zero field. The sharp line at 2.808 eV, which dominates the spectrum at early times, is from recombination of free excitons (FX's). The broad PL line at lower energy, which we have identified as an EMP, forms out of the excitonic state and moves within 1 ns to 30 meV below the FX line. The FX's decay away quickly, leaving at later times the EMP line that completely dominates the spectrum. Time-resolved PL spectra in the 4% MQW are similar, except that the luminescence intensity of the EMP is much weaker (see below), and the binding energy of the EMP is half that observed in the 14% MQW. No evidence for polaronic effects is seen in the 2% sample, presumably because the EMP is not stable in a sample of such low concentration.

In Fig. 2 we show the evolution of the energy position (relative to the FX) of the EMP PL peak with time for both the 4% (squares) and 14% MQW (circles) samples.

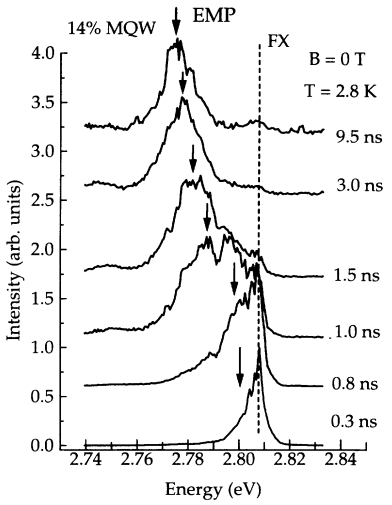

FIG. 1. Time-resolved photoluminescence spectra from the 14% $Zn_{1-x}Mn_xSe/ZnSe$ quantum wells in zero field at 2.8 K following excitation by a 3547-A excitation pulse. The narrow feature seen near 2.805 eV in the spectra from 0 to 1.5 ns after the laser pulse is from recombination of free excitons. The broad feature at 2.77 eV (30 meV below FX) seen at later times is from recombination of the exciton magnetic polaron (EMP).

The solid lines are an exponential fit to the data, and show that the EMP forms much more quickly in the 4% MQW (300 ps) than in the 14% MQW (670 ps). This is in contrast to what Mackh *et al.*[24] observed in $Cd_{1-x}Mn_xTe$ epilayers, where the formation time of polarons *decreased* with increasing Mn concentration. We believe that the formation time of the EMP is longer in the 14% MQW because the hole is more strongly localized to the ZnSe, and so the overlap with the Mn spins in the barriers is weaker. In contrast, the conduction and valence bands are effectively flat across the $Zn_{1-x}Mn_xSe/ZnSe$ layers in the 4% MQW, and so the hole overlaps strongly with the Mn ions.

Time decays of the FX and EMP photoluminescence in the 14% MQW and 4% MQW are shown in Figs. 3(a) and 3(b), respectively. In each case (solid lines) the free-exciton lifetime is less than 150 ps. However, the lifetimes of the EMP's in the 4% and 14% samples are significantly different. While all of the carriers associated

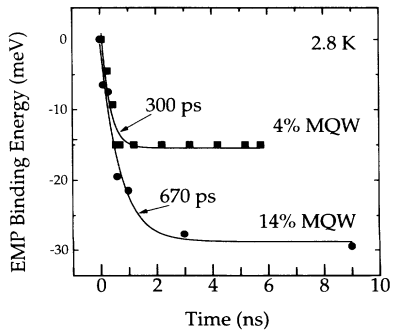

FIG. 2. Plot of the peak energy positions of the EMP (relative to FX) in the 4% and 14% samples as a function of time after photoexcitation. The solid lines are fits of the data to an exponential decay.

with the EMP decay away in the 4% MQW before the arrival of the next excitation pulse, the recombination lifetime of the EMP in the 14% MQW is quite long—over 50% of the carriers excited from one laser pulse survive to see the arrival of the next laser pulse. This results in the large time-integrated PL background seen in Fig. 3(a). Modeling the PL time decays of Fig. 3 using simple rate equations indicates that the EMP lifetime in the 14% MQW is longer than 20 ns, while that seen in the 4% MQW is only 450 ps. In contrast, previous work in bulk crystals or thick films[24–27] and quantum wells[20,21] found that the formation time of the EMP in bulk and quantum systems was comparable to the recombination lifetime.[28] It is not certain in such cases that the EMP ever achieves equilibrium. However, because the spatially indirect EMP in these samples forms in a time much less than the recombination lifetime, the fact that the indirect EMP is in equilibrium with the lattice and magnetic impurities cannot be questioned. This important result opens the door to future experiments to study the EMP in equilibrium with the lattice and magnetic impurities, which before have been impossible to perform.

By acquiring time-resolved spectra as shown in Fig. 1 at a series of temperatures, we can determine the temperature dependence of the EMP binding energy relative to the FX in the 4% MQW (squares) and for the EMP at *equilibrium* in the 14% MQW (circles) as shown in Fig. 4. Note that because we are unable to extrapolate the binding energy of the EMP at high temperatures, we are unable to determine whether or not the EMP described here forms from an impurity-bound exciton, or a free exciton. In spite of this, it is clear from the data that the binding energy of the EMP *relative to the FX* is nearly 30 meV at 2.8 K, and decreases monotonically with temperature. The spatially indirect EMP completely disappears at temperatures above 45 K. Time decays of the EMP in the 14% MQW show that the lifetime of the EMP decreases somewhat over this temperature range, consistent with decreased localization. Above 45 K, the long-lived state disappears, and one only observes short-lived FX with a recombination lifetime less than 150 ps. In contrast, the EMP in the 4% MQW is less bound and disappears at a lower temperature (24 K) than that in the 14% MQW, consistent with the lower Mn concentration in the magnetic layers.

A complete description of the formation and decay of EMP's necessarily involves the dynamics of both the excitons and the magnetic ions. Because the EMP is formed through relaxation of the initially disordered Mn ions in the vicinity of the exciton to a low-energy (polarized) state, the formation time for both the type-I and type-II EMP's must be proportional to the spin-lattice relaxation time. However, the decay dynamics of the Mn-ion polarization are considerably different in the two cases. The excitons composing the type-I EMP recombine with a lifetime that is comparable to (or shorter than) the spin-lattice relaxation time (approximately 400 ps, estimated from measurements described in Ref. 20 on a similar concentration $Cd_{1-x}Mn_xTe$ sample), so that the net magnetization of the Mn ions is limited by the carrier lifetime and furthermore decays (becomes disordered) through spin-lattice relaxation. In contrast, because the lifetime of the type-II EMP (20 ns) is longer than the spin-lattice relaxation time (approximately 400 ps), the magnetization of the local Mn ions will achieve a steady-state net polarization with individual Mn ions flowing in and out of alignment with the EMP. The relaxation time of the Mn-ion polarization thus will be determined mainly by the type-II exciton recombination lifetime. This situation is strikingly different from results reported to date.

An interesting comparison may be made with the recent work of Awschalom *et al.* on EMP dynamics in $ZnTe/Cd_{1-x}Mn_xSe$ quantum wells.[21] Whereas in this paper we directly measure the exciton kinetics and infer the dynamics of the Mn ions, Awschalom *et al.* directly measure the magnetization of the Mn ions and infer the exciton dynamics. In addition, the type-II band alignment of the $ZnTe/Cd_{1-x}Mn_xSe$ heterostructures is the inverse of the $Zn_{1-x}Mn_xSe/ZnSe$ structures discussed here: the *electron* is confined to the magnetic

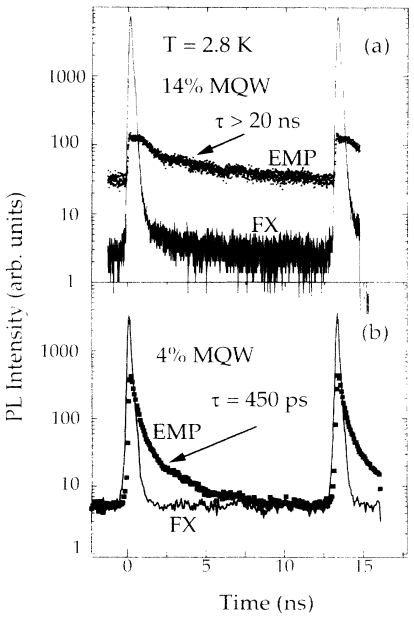

FIG. 3. (a) Time decays of the FX (solid line) and EMP (circles) PL in the 14% MQW plotted on the same relative scale. (b) Same as (a) except for the 4% MQW.

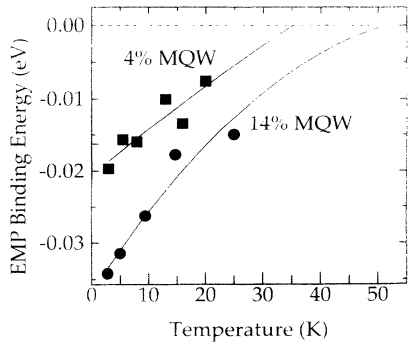

FIG. 4. Plot of the equilibrium binding energy of the EMP for the 14% (circles) and 4% (squares) samples as a function of temperature.

$Cd_{1-x}Mn_xSe$ layers, while the *hole* is confined to the nonmagnetic ZnTe layers.[22] In contrast to the type-II EMP reported here, Awschalom *et al.* measured a decay time that is comparable to the formation time, which indicates either that the lifetime of the exciton associated with the dynamic magnetization is short, or that the EMP itself is unstable and has a short lifetime. Indeed, one expects the type-II EMP in the $ZnTe/Cd_{1-x}Mn_xSe$ system to be less stable than in the $Zn_{1-x}Mn_xSe/ZnSe$ system, since the EMP in the former system is formed by only the electron-Mn exchange which is five times smaller than the hole-Mn exchange. In either case the 400-ps lifetime of the type-II EMP in the $ZnTe/Cd_{1-x}Mn_xSe$ is not sufficient to achieve equilibrium between the carriers and the Mn ions. This is in dramatic contrast with the type-II EMP reported here with the hole confined to the $Zn_{1-x}Mn_xSe$ layers and a recombination lifetime of 20 ns, nearly 40 times the EMP formation time.

In conclusion, we have shown that both the structure and dynamics of EMP's depend strongly upon the Mn concentration in $Zn_{1-x}Mn_xSe/ZnSe$ quantum wells. The time evolution, temperature dependence, and concentration dependence of PL from these structures is consistent with the three types of EMP's proposed in the introduction. At low Mn concentrations ($\approx 4\%$) the exchange energies for *both* the electron and hole are sufficient to overcome the small confinement energies. A type-I EMP is formed with *both* the electrons and holes confined to the $Zn_{1-x}Mn_xSe$ layers. The EMP forms within 300 ps and decays rapidly with a 400-ps recombination lifetime. In contrast, at intermediate Mn concentrations (approximately 14%) only the hole exchange energy is sufficient to overcome the built-in confinement energy, and a type-II EMP is formed with the electron confined to the nonmagnetic ZnSe and the hole confined to the magnetic $Zn_{1-x}Mn_xSe$ layers. The EMP forms within 800 ps (comparable to the spin-lattice relaxation time) but decays slowly with a recombination lifetime in excess of 20 ns. The long recombination lifetime is consistent with the strong spatial separation of the electrons and holes, and allows a significant fraction of the EMP's to achieve thermal equilibrium.

We would like to acknowledge helpful discussions with S. Lance Cooper, and Athos Petrou. L.M.S. and C.D.P. wish to acknowledge the generous support of the NSF under Grant No. NSF DMR94-09049, and the Department of Physics and the University Research Council at the University of Cincinnati for this work. One of us (B.T.J.) also wishes to acknowledge the support of the Office of Naval Research.

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