Formation of the Bound Magnetic Polaron in (Cd,Mn)Se

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Strong evidence for the formation of a bound magnetic polaron in n-$Cd_{0.90}Mn_{0.10}Se$ has been obtained from time-resolved experiments by picosecond laser spectroscopy. In particular, time-varying Stokes shifts associated with a neutral donor bound exciton have been measured to follow the evolution of the polaron at $T = 2$ K. From analysis of data a formation time of approximately 400 psec is inferred for the conditions of the experiment.

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An area of recent interest in the study of semimagnetic mixed II-VI compound semiconductors concerns the behavior of electrons and holes when localized at shallow impurity sites in these alloys. In the case of $Cd_{1-x}Mn_xSe$, for example, large spin splitting of an electron at a donor (D^0) has been observed by spin-flip Raman scattering in the absence of an externally applied magnetic field.[1,2] Elsewhere, results obtained by photoluminescence for the neutral acceptor in $Cd_{1-x}Mn_xTe$ have showed a pronounced increase in the binding energy of the hole on lowering the sample temperature.[3,4] Such anomalous effects have been explained by considering the Heisenberg exchange interaction of the charge carrier spin with the Mn^{2+}-ion localized $3d$ electrons within its Bohr orbit. Golnik *et al.*[3] suggested that the exchange interaction would lead to the formation of an ordered spin arrangement about the impurity ion, introducing the concept of the bound magnetic polaron (BMP) used earlier in analysis of transport data in europium chalgeconides. Physically, a gain in the energy of the impurity complex was expected with the carrier aligning the Mn^{2+}-ion spins within its orbit. Subsequently, Dietel and Spalek,[5] Heiman, Wolff, and Warnock,[6] and Mauger[7] have performed detailed calculations for the BMP effect associated with a neutral impurity. In addition, they have shown how the exchange-induced energy shifts also have a component from a net magnetization present in the finite-size cluster defined by the impurity Bohr volume. This latter contribution by the "thermodynamical fluctuations" has now in fact been shown to dominate the spin splitting and linewidth broadening for the neutral donor in n-$Cd_{1-x}Mn_xSe$ ($x = 0.10$) especially for $T \gtrsim 10$ K.

In this communication we present results where for the first time evidence for the formation of a BMP is directly obtained in time-resolved experiments by picosecond laser spectroscopy. In particular, we have examined the time evolution of spectra associated with the neutral donor bound exciton in n-$Cd_{0.90}Mn_{0.10}Se$. Recent results from cw photoluminescence work in $Cd_{1-x}Mn_xSe$ by Huber *et al.* have shown how the BMP contribution to the energy of a neutral donor bound exciton is likely to be significantly larger than that for the neutral donor.[8] This is attributed to the smaller effective Bohr radius of the exciton and the larger exchange constant for the (outer valence) hole, and manifests itself in a large additional low-energy shift of the bound-exciton luminescence peak for $x = 0.10$ composition as the temperature is lowered from 10 to 2 K. Furthermore, a significant apparent linewidth broadening was measured. In the interpretation of Ref. 8 this behavior reflects the transition of the bound-exciton-spin complex from the thermodynamic-fluctuation-dominated regime to the bound-polaron regime. In the work reported here, we show evidence for the formation of a BMP associated with the bound exciton and connect the measured formation time to the Mn^{2+}-ion spin-spin relaxation processes.

The experimental arrangement employed to perform time-resolved spectroscopy is based on the use of two synchronously pumped, wavelength-tunable dye lasers in an excite-probe configuration, as detailed elsewhere.[9] In the present instance, a picosecond pulse of excitation promotes a low density of bound excitons (on the order of 1×10^{14} cm^{-3}). The presence of this excitation is measured by a weak time-delayed probe pulse as an induced change in its transmission $[\Delta T(\omega)/T(\omega)]$ through the illuminated sample volume. Under circumstances considered here and for $\Delta T > 0$, the dominant contribution to such optically modulated probe signals is directly proportional to the number of donor sites occupied by the excitons at a given instant of time and energy. This follows by noting that $\Delta T/T \sim -\Delta\alpha l \sim \Delta N_{ex}$

$\times f(\omega) l$ where ΔN_{ex} is the exciton density, $f(\omega)$ a line-shape function, and l the sample thickness.

The measurements described here were made while immersing thin platelets (100 μm) of *n*-$Cd_{0.90}Mn_{0.10}Se$ in superfluid helium in the absence of any external magnetic field. The samples were known to have a donor density of $N_d \sim 3\times 10^{16}$ cm^{-3} from Hall measurements. They had earlier been used in spin-flip Raman[6] and luminescence[8] experiments. The low excitation density, corresponding to an average laser power at most 1 mW in a spot size of 100 μm, was necessary to prevented excitonic saturation effects from occurring and was estimated to induce sample heating at most by 1 K. Both the pump and the probe beams were polarized perpendicular to the *c* axis of the crystals (determined by standard x-ray diffraction) to avoid birefringence-induced temporal delays in our measurements. Similar arrangements were employed by us recently to examine the bound-exciton kinetics in these samples at 10 K where exciton thermalization and relaxation were measured, together with a demonstration of the inhomogeneous character of the bound-exciton line.[10]

Figure 1 summarizes the main features in our data at $T = 2$ K and shows modulated probe transmission spectra recorded at different delays (following the excitation at $t = 0$) at a photon energy of $\hbar\omega_{ex} = 1.968$ eV, somewhat below the free-exciton energy. The spectra have been properly normalized by accounting for the variation in the absorption coefficient, void of any fine structure.[10] By making comparisons with steady-state luminescence spectra,[8] observations from our earlier time-resolved work at higher temperatures, and particularly the appearance of a distinct peak in the *excitation* spectrum at short time delays,[10] we can unambiguously assign the spectral features shown to a bound-exciton complex. The initial formation of a bound exciton for such an excitation energy was confirmed to be rapid ($\lesssim 20$ psec) on the time scale of interest here. Most importantly, the data in Fig. 1 show a clear *time-dependent* shift in the probe spectra. In remarkable contrast, we found that the time-resolved spectra observed at 10 K and above (as illustrated in Ref. 10) exhibited *no* measurable shifts but merely a time-dependent amplitude, consistent with the formation and decay of an energetically stationary bound exciton. This constant spectral position of the peak of the modulated transmission at 10 K is shown as the dashed line in Fig. 1. At 2 K we measure an overall red shift in excess of 10 meV within the 800-psec range of our experimental setup. Figure 2 shows the position of the probe spectral peaks as a function of the delay. A good fit to the data can be made with a single exponential time constant of 400 psec. At the same time, the measured signal-amplitude decay indicates a lifetime for the bound exciton complex of some 600 psec. The latter is longer by approximately a factor of 3 than a similarly measured lifetime at 10 K.

An additional crucial observation is related to the dependence of the probe spectra on the excitation energy. At all temperatures monitored, a

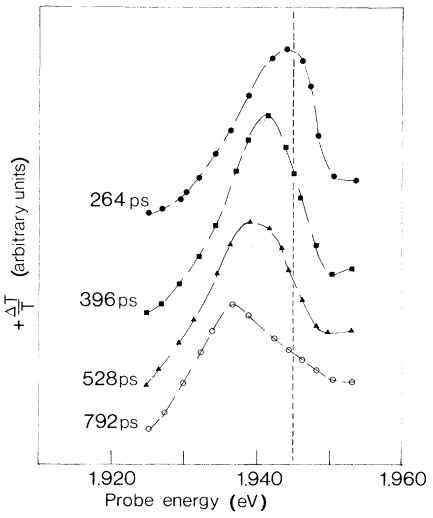

FIG. 1. Modulated transmission spectra for the bound exciton in $Cd_{0.90}Mn_{0.10}Se$ at 2 K as a function of excite-probe delay in picoseconds ($\hbar\omega_{ex} = 1.968$ eV). Interpolation of data appears as the dashed line. Relative amplitudes are not fully normalized with each other in this representation. Vertical dashed line denotes the position of the spectrally stationary peak at 10 K.

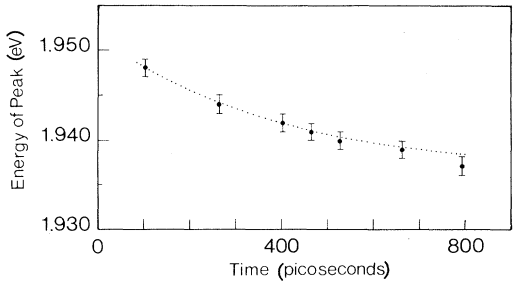

FIG. 2. Energetic position of the peak of the exciton line as a function of delay. Excitation energy in each case is 1.968 eV. Dotted line shows a simple exponential fit.

resonancelike feature appeared in the excitation spectrum (as shown at 10 K in Ref. 10). At 2 K, this enhancement had an approximate low-energy limit at about 1.945 eV, below which the probe spectra of Fig. 1 decreased precipitously in amplitude. This provides direct evidence that the time-dependent behavior in Fig. 1 involves a dynamic self-energy relaxation of a bound-exciton state *only initially* accessible for excitation. Some small-amplitude probe signals could be seen when exciting at further lower energies but these contributed to much broader spectra which were also temporally distinctly separate from the bound-exciton kinetics. They appear likely to be connected to localization phenomena from alloy potential fluctuations, coupled with other impurity-related effects, probably responsible also for the observed absorption-edge broadening.

We believe that the above observations provide strong evidence for the existence of a bound magnetic polaron in a semiconductor from a direct measurement of its dynamics of formation. The time-dependent Stokes shifts evident in Fig. 1 are here interpreted as corresponding to the different stages of the evolution toward spin ordering about the impurity sites. The occurrence of "polaronic relaxation" is also clearly indicated by the experimental ability to couple excitation directly only to the initial "bare" (spin-uncorrelated) bound-exciton state. When comparing the steady-state photoluminescence spectra of Huber *et al.*[8] at 2 K with those in Fig. 1, we find good agreement with their results when *time integrating* our spectra. This explains the puzzle connected with the anomalously broad linewidths reported in Ref. 8. Furthermore, at a higher temperature of 10 K the transient (instantaneous) and steady-state spectra are in mutual agreement while showing frustration of full polaron formation due to thermal disorder.

Dynamically, the BMP formation can be viewed as an evolution of the bound exciton from an initial statistical regime where a thermally fluctuating individual Mn^{2+}-ion spin has no correlation with the charge carrier spin. To first order the carrier here is represented by the outer hole of the bound exciton. (Our experiment is sensitive to such fluctuations since a large number of laser pulses are used to accumulate each data point.) An inhomogeneously broadened optical linewidth, associated with transitions originating from a distribution of perturbed and spin-split levels is then expected from alloy compositional fluctuations.[8] In the transient experiment such an initial state is prepared by the excitation from an applied laser pulse. At 2 K, the exchange interaction between the carrier spin and those of the ion leads to a mutually correlated spin alignment, the BMP, which in the notation of Ref. 5 can be expressed as an effective magnetization of the form $M(r) = \eta \exp(-2r/a_x)$, where η is a variationally determined amplitude and a_x the self-consistent Bohr radius of the carrier (in the hydrogenic envelope approximation). The dynamic evolution of the spectra of Fig. 1 is a direct measurement of the development of such magnetization. In the one-electron (hole) model the mean energy shift E_m associated with the lower spin-split level of the exciton can be calculated from the model of Dietel and Spalek in the BMP (mean-field) limit as[5]:

$$E_M = \beta^2 \chi \tanh(E_M/2kT)/(32\pi g^2 \mu_B{}^2 a_x{}^3), \qquad (1)$$

where β is the exchange constant for the outer hole, χ the susceptibility and a_x the Bohr radius. Quantitatively, we find a reasonable agreement of our data with the predicted energy shifts for the formation of the BMP in $Cd_{0.90}Mn_{0.10}Se$. More specifically the BMP contribution adds approximately 15 meV to the exciton binding energy for an assumed Bohr radius of 30 A by using an exchange constant of $-\beta N_0 = 1.15$ eV[11] where N_0 is the number of cations per unit volume. Here we assume that the final state associated with the probe laser transition, i.e., the neutral donor, experiences a much smaller energy shift as shown earlier.[6,8] In the BMP regime, the alloy compositional fluctuations are still expected to contribute to inhomogeneous linewidths which remain rather broad. One potential complication affecting these estimates concerns the possible participation of the inner pair of electrons in the exchange interactions. Conceivably, the large effective internal magnetic fields (well in excess of 100 kG) could alter the bound exciton configuration from that assumed by us.

The time constant measured for the formation of a BMP (Fig. 2) can be compared with available experimental data for spin-spin relaxation in $Cd_{1-x}Mn_xSe$. While for $x \lesssim 0.10$ such Mn-Mn ion interaction may be included as a small correction in the development of the BMP theory,[5,6] it is likely to dominate the formation time of the spin aligned complex, under the assumption of a much faster inherent hole (electron) spin flip. Among others, Oseroff[12] has made recent measurements of spin susceptibility and electron-spin resonance of the Mn^{2+}-ion in $Cd_{1-x}Mn_xSe$. At low

temperatures the Mn-Mn spin interaction (antiferromagnetic) leads to a strongly temperature-dependent ESR linewidth broadening. For the paramagnetic $x = 0.10$ composition, a simple connection may be made with the measured ESR linewidths and the experimentally observed BMP formation time. In particular, we extrapolate a spin-spin dephasing time (T_2) of approximately 100 psec from the data in Ref. 12, in the temperature range of interest. This would represent a lower bound for the formation time of a BMP and is thus in a general range of agreement with our results. As the spin splitting develops, spin-lattice relaxation (T_1) is expected to add to the formation time. The calculation of a more accurate formation time would have to account for the influence of the inhomogeneous, time-evolving magnetization $M(r)$, as the spin alignment is taking place within the renormalized exciton Bohr volume.

In conclusion, we have obtained strong evidence from direct time-resolved measurements for the evolution of a photoinduced BMP associated with an impurity bound exciton in $Cd_{0.90}Mn_{0.10}Se$. These results can be connected to previously measured cw photoluminescence spectra which provide a time-integrated contrast to our spectra. While reasonable quantitative agreement exists between experiment and estimates for the BMP energy and formation time in a simple one-particle approach, questions remain concerning the exciton configuration in the BMP limit and the contribution to its formation time by collective spin effects.

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