

Transient-level crossing of free and bound excitonic magnetic polarons in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ single crystals

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(Received 14 June 2000; published 29 March 2001)

We investigated the dynamics of free and bound excitonic magnetic polarons in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.03$) single crystals by time-resolved photoluminescence experiments. We found that the magnetic polarons formed from free excitons are more stable than those formed from bound excitons. As a consequence, the peak energies of the optical emissions of free excitons and donor-bound excitons cross in the time-resolved photoluminescence spectra. Furthermore, we observed that nonmagnetic localization is not required to form free magnetic polarons.

DOI: 10.1103/PhysRevB.63.153314

PACS number(s): 78.47.+p, 71.20.Nr, 71.10.Pm, 71.35.Lk

Many discussions have taken place in the last 20 years about the formation of magnetic polarons (MP's) in diluted magnetic semiconductors (DMS's).¹⁻¹⁴ MP's are entities where the band electrons (or the excitons) couple to the localized spins of the magnetic elements through the exchange interaction. This results in the polarization of the localized spins of the magnetic ions within the Bohr radius of the MP. For the realization of this coupling, it is necessary that the carriers become localized. A convincing experimental proof of the formation of MP from an electron bound to a donor (D^0 complex) is the finite spin-flip energy detected for the electron of D^0 at zero magnetic field by spin-flip Raman-scattering experiments.² In contrast to bound magnetic polarons (BMP's), "free" magnetic polarons (FMP's) are formed when free excitons are trapped in the exchange potential well created by the spin fluctuations of the Mn^{2+} ions.^{3,4} The concept of "free" MP does not necessarily mean that the FMP is a mobile complex. It rather means that the MP is formed from a free exciton (FX). But for the formation of FMP's, it is necessary that the FX's are localized long enough to polarize the Mn spins in the polaron. It is not clear at present whether a nonmagnetic localization of the FX is required for the formation of a FMP [in this case, one speaks about "localized" magnetic polaron (LMP's) (Refs. 5 and 6)]. We show in this work that FMP's can form also in the absence of any nonmagnetic localization process. Excitonic MP's have been studied extensively by photoluminescence (PL) experiments. Golnik, Ginter, and Gaj⁷ reported the observation of the formation of MP's from acceptor-bound excitons and FX's in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals in the temperature dependence of the PL spectra. Furthermore, it is essential to study the kinetics of the MP formation because the lifetime of bound excitons is as short as few nanoseconds in DMS's, and the lifetime of FX's is only about 500 ps in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. Time-resolved PL experiments offer a good opportunity to study the dynamics of the MP formation.⁸ Zayhowski *et al.*⁹ studied the recombinations of donor-bound excitons (D^0, X) and FX's in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ crystals by time-resolved PL experiments. Oka *et al.*¹⁰ reported the dynamics of FMP formation by time-resolved PL experiments.

After intensive experimental and theoretical studies about the FMP in DMS materials,¹¹⁻¹³ there is still controversy

about the stability of free excitonic MP's. In fact, FMP's are believed to be less stable than BMP's (Ref. 14) because of the kinetic energy arising from the confinement of the FX's in the exchange potential wells of the Mn spin fluctuations. In this work, we compare directly the dynamics of the MP's formation for BMP and FMP in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals with $x=0.03$ by time-resolved PL experiments. For the BMP, we focus on the (D^0, X) complex, consisting of a positively charged impurity center, two electrons with opposite spin and a hole. Because of the large hole mass, the (D^0, X) complex is similar to a H_2 molecule. The magnetic properties of the (D^0, X) complex in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ depend mostly on the hole spin. Similarly, the magnetic properties of a FX also depend mostly on the hole spin. Therefore, the (D^0, X) complex allows for a direct comparison between BMP and FMP. The only difference between the (D^0, X)-BMP and the FMP is the degree of localization of the hole. In this letter, we show that FMP's have a larger binding energy than (D^0, X)-BMP's because the self-trapping of the hole in the potential of the Mn^{2+} spin fluctuations is more effective for a FMP than a (D^0, X)-BMP.

High-purity $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ single crystals with several Mn compositions were prepared by the vertical Bridgman method. Materials of each element were enclosed in a carbon-coated quartz ampoule. For the PL experiments, we chose the samples with $x=0.03$ because this is the composition for which the PL signals of the FX and the (D^0, X) complex are most clearly resolved. The sample thickness was 1 mm. For the optical excitation, we used a wavelength tunable femto-second pulsed laser. The excitation wavelength was 400 nm and the pulse duration was 120 fs with a repetition rate of 86 MHz. The pulse energy density was below 5 nJ/cm^2 . A streak camera was used to record the time variation of the exciton luminescence. The samples were immersed in liquid helium at 4.2 K and were kept in the center of a magnet allowing for fields up to 7 T.

In Fig. 1, we show contour plots of the time-resolved PL spectra of a $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$ crystal measured at magnetic fields of 0 and 7 T. The PL spectra show two peaks. One of them is sharp, while the other one is broad and shows a strong transient energy relaxation. We assign these two

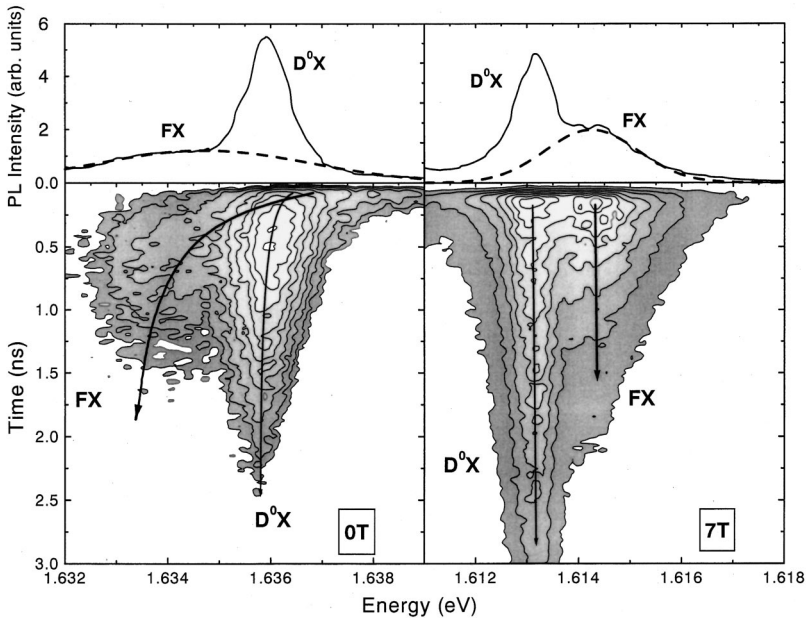


FIG. 1. Time-integrated PL spectra at 0 and 7 T (top) and transient PL contour plots (bottom) in $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$.

peaks to the signals of the (D^0, X) and the FX, respectively. FX becomes stronger with increasing Mn concentration and it is the only PL signal observed for x above 0.06, as the bound excitons are no longer observed.

At zero field, we observe the transient level crossing of the FX peak and the (D^0, X) peak (Fig. 1). This occurs in consequence to the large energy relaxation of the FX. A similar double-peak structure was found in the time-integrated PL spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ crystals with $x = 0.05, 0.10,$ and 0.20 .⁹ Zayhowski *et al.*⁹ assigned the two peaks to the recombinations of the FX and (D^0, X) . In the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ sample, in which the double-peak PL structure was observed most clearly ($x = 0.10$), some indications of a level crossing of the FX and (D^0, X) peaks were found comparing the different temperature dependences of the two PL peaks.⁹ But, on the basis of these observations, a clear assignment of the FX and (D^0, X) peaks in the PL spectrum of $\text{Cd}_{0.90}\text{Mn}_{0.10}\text{Se}$ crystals could not be made.⁹ In Fig. 1, the transient level crossing between the PL emissions of the FX and (D^0, X) is observed at 190 ps after the optical excitation. The temporal evolution of the two peaks is displayed in Fig. 1 by a solid line with arrows. With increasing magnetic field, both emission peaks shift to lower energies due to the giant Zeeman splitting of DMS's.¹ From the field dependence of the PL spectra, the effective g value of the main emission peak is estimated to be $g_{\text{eff}} = 113$ (neglecting the effect of the MP). At zero field, both PL signals show clearly a transient energy relaxation (Fig. 1). In contrast, in a field of 7 T, the energy relaxation of both peaks vanishes (Fig. 1). As a result, no level crossing between the FX and (D^0, X) peaks is observed at 7 T. Furthermore, at 7 T the FX's emission peak is observed at 1 meV above the (D^0, X) peak, similar to the situation occurring in CdTe.¹⁵ This indicates that the anomalous level crossing and the strong FX energy relaxation observed at zero field arises as a consequence of FMP formation. After the FX is trapped in the exchange potential well of the fluctuating Mn spins, the $sp-d$ exchange interaction stabilizes the MP by orienting the Mn spins. This process

yields the transient energy relaxation observed at zero field in Fig. 1.

To analyze the energy relaxation of the two PL peaks, we integrated the transient PL spectra within time intervals of 20 ps and plotted the integrated spectra in Fig. 2 for three time delays. The PL spectra feature a sharp peak of the (D^0, X) signal superimposed on a broad peak of the FX's recombinations. These PL spectra can be decomposed into two-Gaussian peaks. The fit curves are included in Fig. 2. The halfwidth of the narrow peak is constant. Instead, the width of the broad FX peak first increases as the FX's are localized in exchange potential wells of different depths $-\beta \sum_i \mathbf{S}_i \cdot \mathbf{J} |\varphi(r)|^2$ and then decreases slowly with time, when the Mn^{2+} spins are aligned in the MP's and all the localizing

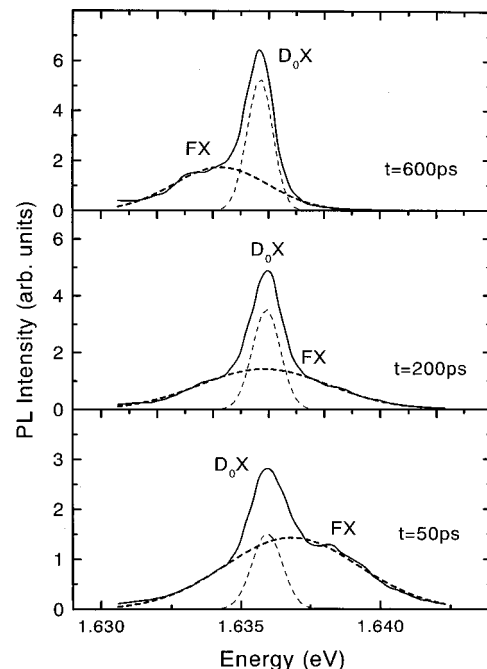


FIG. 2. Two components in the time-resolved PL spectra fitted by two Gaussian peaks.

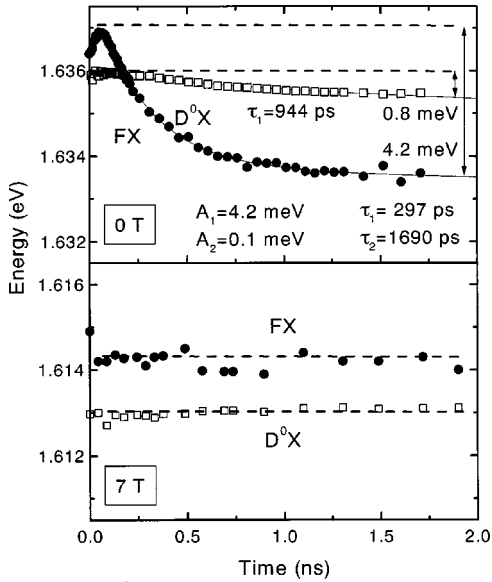


FIG. 3. Time dependence of the PL peak energy in the time-resolved spectra. The upper figure was measured in zero field and the lower figure at $H=7$ T.

exchange potential wells are leveled off to the same depth. For the exchange potential well, β is the p - d exchange interaction energy, the summation runs over the localized Mn spins \mathbf{S}_i in the polaron and $\mathbf{J}(\vec{r})$ is the total angular momentum of the hole in the FX with wave function $\varphi(r)$.

The energy relaxation and the energy crossing of the FX and the (D^0, X) peaks are presented in detail in Fig. 3. The FX peak crosses the (D^0, X) at the time delay of 190 ps. In the first 50 ps, the peak energy of the FX signal measured at zero field increases slightly and then decreases following a double exponential decay law with the decay constants $\tau_1 = 297$ ps and $\tau_2 = 1690$ ps. The initial rise of the transient energy relaxation is not fully understood. But it is probably not related to the MP formation, since it is detected also in CdTe.

The slow energy relaxation component with decay time τ_2 represents the nonmagnetic localization of the FX's in the alloy potential fluctuations and has a very small amplitude ($A_2 = 0.1$ meV). The nonmagnetic localization energy measured in a field of 7 T lies below 0.1 meV for both PL peaks (Fig. 3). This indicates that the nonmagnetic localization in the alloy potential fluctuations is negligibly small in $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$. Therefore, the transient PL energy relaxations of 0.8 and 4.2 meV detected at zero field for (D^0, X) and FX, respectively, have a purely magnetic origin and nonmagnetic localization is not required to form a MP. In fact, our value of 4.2 meV for the binding energy of the FMP in $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$ is larger than the theoretical value of 1 meV,¹³ and is in good agreement with the experimental value of 3.3 meV observed for the $x=0.18$ crystals.¹¹ For (D^0, X) , the time dependence of the PL peak energy follows a single exponential decay law with a long decay time $\tau_1 = 944$ ps, indicating that the MP formation process takes more time for BMP's than for FMP's (297 ps for FMP's in $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$). From the temperature dependence of the PL spectra of $\text{Cd}_{0.952}\text{Mn}_{0.048}\text{Te}$ crystals, Bukivskii *et al.*⁴ observed a spin splitting of 0.8 meV at 4.2 K for the (D^0, X)

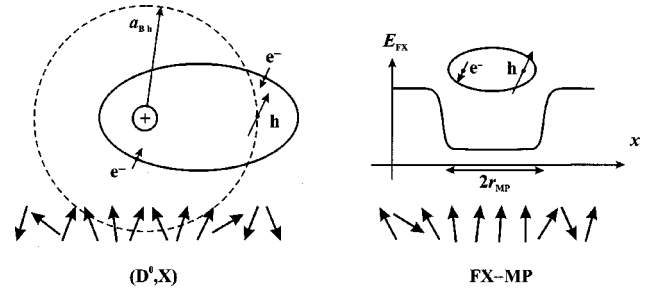


FIG. 4. Schematic diagram for the (D^0, X) -BMP and the FMP. The thick arrows at the bottom represent the Mn^{2+} spins.

complex. This is in perfect agreement with our results (Fig. 3).

At 7 T, no crossing between the (D^0, X) and FX levels is observed. The mechanism of localization of the FX in the exchange potential wells created locally by the favorable alignment of the Mn^{2+} spin fluctuations^{2,3} is inhibited because the Mn^{2+} spins are aligned in the field. In this case, there is no longer the possibility of having a *local* exchange potential well, as it is occurring at zero field due to the Mn^{2+} spin fluctuations. Therefore, at 7 T there is no trapping potential anymore for the excitons and the positions of the (D^0, X) and FX levels are as in CdTe, although with a different energy gap of the host material and a different Zeeman shift of the bands. In fact, at 7 T the FX's emission peak is observed at 1 meV above the (D^0, X) peak, similar to the case of CdTe.¹⁵

From the analysis (described below) of our data of the transient PL energy relaxation observed at zero field for the (D^0, X) complex and FX's (Fig. 3), we deduce the picture of the (D^0, X) -BMP and the FMP drawn schematically in Fig. 4.

For the energy relaxation measured for the transient PL spectra we write

$$\Delta E = \Delta E_{\text{mag}} + \Delta E_b + \Delta E_{\text{kin}}, \quad (1)$$

as proposed in Ref. 13. Here, ΔE_{mag} is the total Zeeman shift of the electron and hole states, respectively, in the exchange field of the MP. ΔE_b represents the variation of the binding energy with the field as is important for the BMP. $\Delta E_{\text{kin}} = \hbar^2/2m^*(2r_{\text{MP}})^2$ is the confinement energy of the excitons in the exchange potential well of the MP (m^* is the reduced excitonic mass and r_{MP} represents the Bohr radius of the MP). The variation of the terms listed in Eq. (1) during the MP formation is evaluated by minimizing the total free energy of the system.¹³ In the following discussion, we simplify the consideration using the formalism proposed by Golnik *et al.*⁷ This permits to separately estimate the various contributions to Eq. (1). In a (D^0, X) complex, it was found¹⁶ that the variations of the Bohr orbit of the electrons and of the hole during the formation of a BMP are negligible. Therefore, we neglect the ΔE_{kin} term in Eq. (1) for the (D^0, X) -BMP. For the exchange field B_{ex} of the hole in the excitonic MP, we adopt the following form proposed by other authors,^{3,17} where $J=3/2$ for the hole in the exciton, V_{Mn} is the average volume occupied by one Mn ion and V_{MP} is the MP volume:

$$B_{\text{ex}} = \frac{\beta J |\varphi(r)|^2}{3\mu_B g_{\text{Mn}}} = \frac{\beta J}{3\mu_B g_{\text{Mn}} V_{\text{MP}}}. \quad (2)$$

The hole density $|\varphi(r)|^2$ is inversely proportional to the volume of the MP.³ Following now the formalism of Gubarev,¹⁸ and taking into account the fact that in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ the exchange energy of the valence band is four times the exchange energy of the conduction band,¹⁹ we find a PL energy relaxation $\Delta E(D^0, X) = 3\Delta_c/2$ for the (D^0, X) -BMP. In this equation, Δ_c is the Zeeman splitting of the conduction band. For a D^0 complex forming a BMP, the value of Δ_c can be determined by spin-flip Raman experiments.² The value of 0.8 meV determined from the transient PL energy relaxation $\Delta E(D^0, X)$ for $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$ (Fig. 3) is in very good agreement with the value of 0.8 meV determined at 4.2 K for Δ_c from spin-flip Raman experiments carried out in $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ for the D^0 complex. It is remarkable that the D^0 and (D^0, X) complexes have a similar exchange field. Furthermore, we notice that $\Delta E(D^0, X)$ measured in the transient PL spectra is not the binding energy of the (D^0, X) -BMP but it rather corresponds to the difference between the binding energies of the (D^0, X) -BMP and the D^0 -BMP. In fact, the end state D^0 of the PL emission process of the (D^0, X) complex is still spin polarized and can form a BMP.^{17,18} The situation is simpler for the FMP, since the FX annihilates in the PL emission process. For the FMP we find (adopting again the formalism proposed by Gubarev¹⁸) a PL energy relaxation $\Delta E(\text{FX}) = 5\Delta_c/2 - E_{\text{kin}}$. But the Zeeman splitting Δ_c of the (D^0, X) -BMP is different from that occurring in the FMP, due to the different exchange fields of bound excitons and FX. To determine the radius of the FMP, we write $\langle S_{\text{Mn}} \rangle$ as a modified Brillouin function.¹⁹ Then, to a first approximation, $\langle S_{\text{Mn}} \rangle$ is inversely proportional to the volume V_{MP} . Taking the size of 92 Å (Ref. 16) for the hole orbit in the (D^0, X) complex in $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Te}$, one finds from the equations for $\Delta E(\text{FX})$ and $\Delta E(D^0, X)$ that the FX in the FMP has a localization radius $r_{\text{MP}} = 50$ Å. This is in good agreement

with the estimations of Kavokin *et al.*,³ who found that the electron and the hole of a FMP are localized within the same radius by the Mn^{2+} spin fluctuations. The size of the FMP is determined by the size of the exchange potential well trapping the free exciton. In these terms, in the (D^0, X) complex the strong coupling to the donor prevents the hole from being fully trapped in the exchange potential well determined by the Mn spin polarization. As a consequence, the hole of the (D^0, X) complex is not sufficiently localized to produce a strong exchange field and align the Mn spins effectively. In fact, from the Zeeman splitting of the conduction band occurring in a (D^0, X) -BMP, one determines a hole-induced exchange field of only 0.088 T in the (D^0, X) complex. This is much smaller than the exchange field of 0.56 T determined for the FMP.

In summary, we investigated the magnetic polaron formation in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals with $x = 0.03$. We observed the formation of magnetic polarons from the donor-bound excitons with a PL energy relaxation of 0.8 meV. For the magnetic polarons originating from the FX's we observed a binding energy of 4.2 meV. This is observed in a large energy relaxation of the FX peak, which crosses the (D^0, X) peak at 190 ps after the laser excitation. The small binding energy of the (D^0, X) -BMP (compared to the FMP) indicates that the strong coupling of the exciton to the donor impurity prevents the hole to be trapped in the localization potential of the Mn spin fluctuations. It turns out that the FMP has a localization radius of 50 Å, i.e., about one half of the Bohr radius of the hole in the (D^0, X) -BMP. Furthermore, we found that non-magnetic localization is not required to form a FMP. Finally, we comment that the magnetic localization of the FMP is not eternal, as it depends on the orientation of the Mn spins. Therefore, in principle, it does not prevent the FMP to be mobile.²⁰

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