Effect of alloy potential fluctuations on the exciton magnetic polaron in the bulk diluted magnetic semiconductors $Cd_{1-x}Mn_xTe$

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(Received 5 May 2003; revised manuscript received 15 July 2003; published 7 November 2003)

A theory for exciton magnetic polarons (EXMP's) in diluted magnetic semiconductors localized by the *sp-d* exchange interaction with assist of alloy potential fluctuations (APF's) is presented within the molecular-field approximation. First, we show that the self-trapped EXMP in $Cd_{1-x}Mn_xTe$ is rarely realized except at quite low temperatures below ~1 K. Then, we incorporate the effect of APF's with the optimal fluctuation method; the calculated results turn out to be consistent with the photoluminescence data above 1 K observed after band-edge excitation. This strongly suggests the necessity of APF's to localization of EXMP's. The calculation with APF's further demonstrates that the luminescence due to the EXMP in $Cd_{1-x}Mn_xTe$ is observed clearly from $x \sim 0.05$, which is also consistent with the experiment.

DOI: 10.1103/PhysRevB.68.193202 PACS number(s): 75.50.Pp, 78.55.Et

Photoexcitation in diluted magnetic semiconductors (DMS's) may produce microferromagnetic domains in the paramagnetic medium within a lifetime. In this manner, the exitons in DMS's, such as $Cd_{1-x}Mn_xTe$, are strongly affected by the *sp-d* exchange interaction; in some cases, the excitons are localized as self-trapped exciton magnetic polarons (ST-EXMP's). In the last decades, both experimental and theoretical investigations for the EXMP's in DMS's have been performed related to the observed L_2 luminescence.[1] The stability of ST-EXMP's in DMS's, together with the formation mechanism of EXMP's, however, is still a subject of controversy: the recent theoretical study by Miao, Stirner, and Hagston[2] reported that the ST-EXMP in $Cd_{1-x}Mn_xTe$ is stable up to relatively high temperatures ($T \leqslant 30$ K) without any other primary localization. The present author,[3] however, pointed out that the electron-hole pair approximation they used gives a spurious confinement potential for excitons and showed that the ST-EXMP is rarely realized except at quite low temperatures below ~1 K. However, there is a further mechanism that leads to the intrinsic localization of excitons: alloy potential fluctuations (APF's) due to the local compositional fluctuation of magnetic ions,[4] since the DMS is a compound made up in part of substantial magnetic ions. Up to now, few theoretical studies of the effect of APF's on EXMP's have been developed. In this report, we then study the effect of APF's, using the product of the wave functions for the center-of-mass motion and the relative motion of the electron and hole. By this representation, a proper treatment of the attractive Coulomb interaction between electrons and holes is guaranteed.[3]

Before discussing the present subject, we note two points of relevance. First, over the last decade, the bound magnetic polarons (BMP's) in DMS's have attracted considerable attention from the theoretical[5–8] and experimental[1,9] viewpoints. In this case, excess carriers are initially bound to a Coulomb attractive potential of extrinsic donors or acceptors. On the other hand, this paper deals with an intrinsic localization of carriers due to the compositional fluctuation of Mn ions. Second, for EXMP's in DMS's, there seems a marked discrepancy for a Mn concentration dependence of the polaron energy observed by Mackh *et al.*[10,11] and Takeyama *et al.*[12,13] The former determined the polaron energy by selectively excitating at successively lower energies of the APF levels in the band gap until the Stokes shift remained a constant. This constant value was taken as the polaron energy. The latter, however, used the interband excitation or the band-edge excitation technique. Two groups seem to observe different polaron complexes because of the finite lifetimes of EXMP's together with different relaxation processes associated with the excitation technique used. A similar suggestion is given by Hagston *et al.*[14] and the importance of the dynamical effect was experimentally shown by Yakovlev *et al.*[15] In this paper, we deal with the case for the band-edge excitation, but not the selective excitation.

Now, we return to the present subject. To make the effect of APF's clear in the band-edge excitation, we first study the case without APF's and then incorporate its effect; the calculation suggests the necessity of APF's to the localization of EXMP's in bulk $Cd_{1-x}Mn_xTe$ at least above ~1 K. Let us employ the following variation function for EXMP's:

$$\begin{aligned}\phi(\vec{r}_e,\vec{r}_h) &= \phi_g(\vec{r}_g)\,\phi_r(\vec{r}_e-\vec{r}_h) \\ &= \left(\frac{\nu_g\nu_r}{\pi}\right)^{3/2} \exp\left\{-\frac{\nu_g^2}{2}[(1-\delta)\vec{r}_e+\delta\vec{r}_h]^2\right\} \\ &\quad \times \exp\left\{-\frac{\nu_r^2}{2}(\vec{r}_e-\vec{r}_h)^2\right\}. \end{aligned} \tag{1}$$

Here $\phi_g(\vec{r}_g)$ is the wave function for the center-of-mass motion and $\phi_r(\vec{r}_e-\vec{r}_h)$ is for the relative motion of electron and hole: $\vec{r}_g$ is the coordinate of the center of mass, and $\vec{r}_e$ and $\vec{r}_h$ are, respectively, the position vectors for the electron and hole. Furthermore, ν_g means the inverse of the extent of the center-of-mass motion and ν_r that of the relative motion. By the interaction the effective mass may be varied; this is considered by $\delta = m_h^*/(m_e^*+m_h^*)$, where m_e^* and m_h^* are, respectively, the dressed masses for the electron and hole. We thus have introduced ν_g, ν_r, and δ as the variation parameters and adopt the Gaussian function for $\phi_g(\vec{r}_g)$ and $\phi_r(\vec{r}_e-\vec{r}_h)$ as shown in Eq. (1). This variation function was used

by Sumi[16] for studying the interaction between the exciton and acoustic phonon. In $\nu_r^2-\delta(1-\delta)\nu_g^2=0$, Eq. (1) is separable into electron and hole parts: we have an electron-hole pair in such a case.

The total free energy for EXMP's without APF's may be given within the molecular-field approximation (MFA) as[3,5]

$$F[\phi_g,\phi_r,M]=\frac{3}{2}\frac{m}{m_e}E_H\left\{\left[(1-\delta)^2+\frac{\delta^2}{\gamma_0}\right]\nu_g^2+\left(1+\frac{1}{\gamma_0}\right)\nu_r^2\right\}-\frac{4}{\sqrt{\pi}}\frac{E_H}{\varepsilon}\nu_r-kT\ln\left\{2\cosh\frac{\Delta_e}{kT}\right\}-kT\ln\left\{2\cosh\frac{\Delta_h}{kT}\right\}-\frac{kT}{V_p}x_{\rm eff}\int G(M(\vec{r}))d\vec{r}. \quad (2)$$

Here ν_g and ν_r are normalized by he inverse of the Bohr radius. The first term in Eq. (2) is the loss of the transfer energy by the localization of exciton. The second is the attractive Coulomb interaction energy between the electron and hole. The third and fourth terms, which are the driving force for EXMP's, are the free energy by the *sp-d* exchange interaction; Δ_e and Δ_h are, respectively, the spin splitting for the electron and hole defined by

$$\Delta_e=\frac{N_0\alpha}{2}x_{\rm eff}S\int|\psi_e(\vec{r})|^2M(\vec{r})d\vec{r}, \quad (3a)$$

$$\Delta_h=\frac{N_0\beta}{2}x_{\rm eff}S\int|\psi_h(\vec{r})|^2M(\vec{r})d\vec{r}, \quad (3b)$$

in the MFA, where $N_0\alpha$ and $N_0\beta$ are, respectively, the *sp-d* exchange constant for the electron and hole, S is the magnitude of localized Mn spin, $|\psi_e(\vec{r}_e)|^2=\int|\phi(\vec{r}_e,\vec{r}_h)|^2d\vec{r}_h$, $|\psi_h(\vec{r}_h)|^2=\int|\phi(\vec{r}_e,\vec{r}_h)|^2d\vec{r}_e$. The induced magnetization of Mn spin, $M(\vec{r})$, is calculated with a modified Brillouin function (MBF) by $M(\vec{r})=B_S(h(\vec{r}))$, where $B_S(h(\vec{r}))$ is the Brillouin function with the molecular field $h(\vec{r})$ obtained by

$$k(T+\Theta)\times h(\vec{r})=V_p\left\{\frac{N_0\alpha}{2}S|\psi_e(\vec{r})|^2\tanh\left(\frac{\Delta_e}{kT}\right)+\frac{N_0\beta}{2}S|\psi_h(\vec{r})|^2\tanh\left(\frac{\Delta_h}{kT}\right)\right\}. \quad (4)$$

The physical content of the MBF and its limited quality is seen in Ref. 17. The last term in Eq. (2) is the magnetic entropy due to the polarization of Mn spins. m is the free electron mass, $\gamma_0=m_h/m_e$, where $m_e(m_h)$ is the electron (hole) effective mass of the conduction (valance) band, ε the dielectric constant, $x_{\rm eff}$ the so-called the effective Mn concentration characteristic to DMS's,[9] V_p the volume per cation, k the Boltzmann constant, T the temperature, Θ the antiferromagnetic temperature,[9,17] and $E_H=13.6$ eV. By minimizing Eq. (2) with respect to ν_g, ν_r, and δ, we obtain the minimum free energy for EXMP's. On the other hand, the free exciton state is obtained as $\nu_g=0$ and

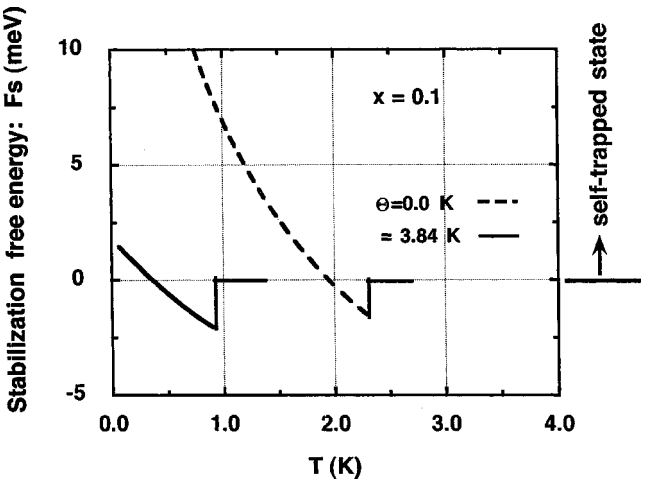

FIG. 1. Stabilization free energy of ST-EXMP's, F_S, for $x=0.1$ is shown as a function of temperature for the case of $\Theta=3.84$ K by a solid line. The ST-EXMP is stable for positive F_S. The case for $\Theta=0$ K is also shown by a dashed line for comparison.

$$\nu_r=\frac{4}{3\sqrt{\pi}}\left(\frac{1}{\varepsilon}\right)\frac{m_h}{m_e+m_h}\frac{m_e}{m}.$$

In the calculation for $Cd_{1-x}Mn_xTe$, the following material parameters are used: $m_e=0.096m$, $m_h=0.60m$,[18] $N_0\alpha=220$ meV, $N_0\beta=-880$ meV,[18] and $\varepsilon=10.6$.[2] Now we examine the possibility of ST-EXMP's for $x=0.1$; from the experiment, $x_{\rm eff}$ and Θ were obtained as 0.039 and 3.84 K for $x=0.1$, respectively.[17] The stabilization free energy F_S, calculated as the free energy difference between EXMP's and the free exciton, is shown in Fig. 1; the ST-EXMP is stable for the positive F_S. We see that the ST-EXMP is stable up to about 0.35 K; between 0.35 and 0.9 K, the ST-EXMP coexists as a metastable state with the stable free exciton; at 0.9 K, the metastable ST-EXMP abruptly changes into the free exciton state; above 0.9 K, only the free exciton exists. The photoluminescence experiments in $Cd_{0.88}Mn_{0.12}Te$, however, certainly show that an energy shift of the L_2 emission associated with a magnetic localization is observed up to $\sim$25 K.[12,13] This means that the calculation without APF's fails to explain the localization of the exciton at such high temperatures, as already shown.[3]

Then the effect of APF's is incorporated next. The study of the density of states in the band gap of solid solutions due to composition fluctuations was developed many years ago.[19,20] Following these theories, the band-edge broadening in solid solutions was also studied.[21] A theory for EXMP's trapped at APF's, however, has not yet been developed as far as the author knows except the one by Hagston *et al.* for selective excitation.[14] This paper is a report of the EXMP's localized by cooperation of APF's after band-edge excitation.

The following analytic approximation for the fluctuation potentials was given by Hagston *et al.*[14] after Lifshitz[20] and Baranovskii and Efros:[21]

$$V_{\rm APF}(r')=-|E|V_0\exp\left(-\frac{r'^2}{\sigma}\right), \quad (5)$$

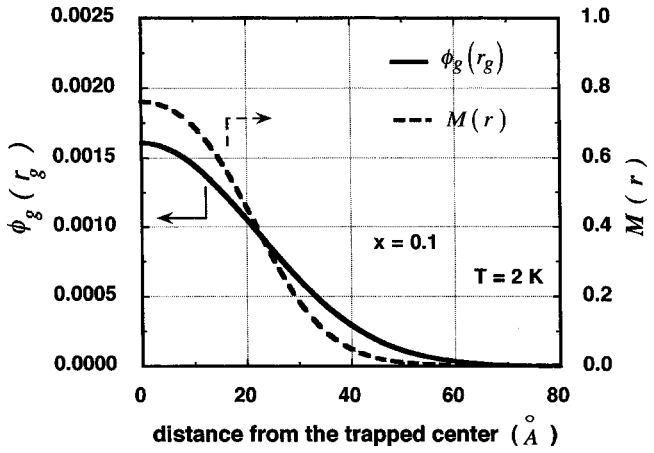

FIG. 2. Profile of EXMP's localized by the assist of APF's calculated at 2 K is shown for $x=0.1$ as a function of the distance from the trapped center. The wave function for the center-of-mass motion, $\phi_g(r_g)$, is shown by solid line with scale on the left y axis, while the magnetization of the Mn spins, $M(r)$, is shown by a dashed line with scale on the right y axis. The unit of the left y axis is $a_B^{-3/2}$, while that of the x axis is angstroms.

where $E<0$ is a localization energy in the band gap and $r'=r\sqrt{2m^*|E|}/\hbar$ with the band mass m^*; $V_0=18.7$ and $\sigma=0.265$. The density of the states in the gap in this model is given by $g(|E|)=g(0)\exp(-\sqrt{|E|/E_0})$, where E_0 is a measure of the band-edge smearing caused by the composition fluctuations. In the present case, the exciton binding energy due to the relative motion is ~10 meV and thus is larger than $|E|$ as later shown. Then we assume that the relative motion of the exciton is not so influenced by APF's; the APF affects the center-of-mass motion, giving a smearing of the band edge or making a localization of the exciton with the small kinetic energy. For a calculation of E_0, the variation rate of the band gap, dE_G/dx, is thus used with the substitution of the total mass, m_e+m_h, for m^*.[21,22] The band-edge smearing is, then, estimated by

$$E_0(x)=\frac{1}{(178\times 16)E_H^3}\left(\frac{dE_G(x)}{dx}\right)^4 \times x^2(1-x)^2\left(\frac{m_e+m_h}{m}\right)^3\left(\frac{d(x)}{a_B}\right)^6, \qquad (6)$$

where $d(x)$ is the cation-cation distance and a_B is the Bohr radius. Using Eq. (6), the broadening of the exciton reflection lines of $Zn_xCd_{1-x}S$ and $Zn_xCd_{1-x}Te$ was well described.[22] Thus we approximate $|E|$ in Eq. (5) by $E_0(x)$. This means that the excitons after the band-edge excitation experience the alloy fluctuation potentials with the localization energies centered at $E_0(x)$ within a lifetime. In this case $E_0(x)$ gives the Stokes shift (SS) at high temperatures within the MFA. Using the experimental values for $Cd_{1-x}Mn_xTe$,[9] we obtain $E_0(x)$ as 0.286, 1.02, and 3.18 meV for $x=0.05$, 0.10, and 0.20, respectively. These values are well correlated to the SS at high temperatures measured from the luminescence data:[1,13] 1 meV at $x=0.12$ and 4 meV at $x=0.18$. Furthermore, we approximate the expectation value of APF's as

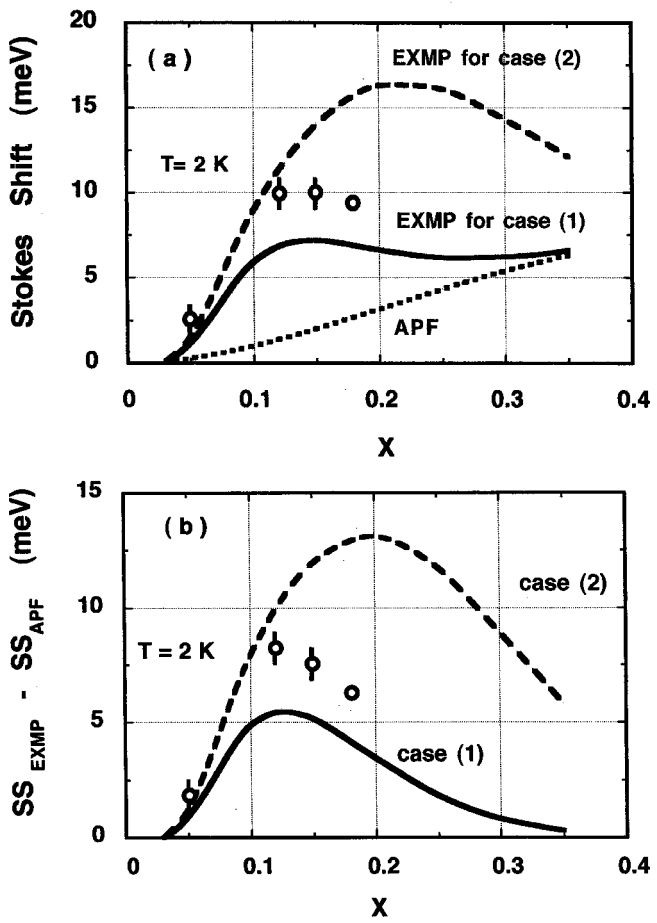

FIG. 3. Calculated Stokes shift (SS) is shown as a function of Mn concentration x in (a) for three cases: the exciton localized by APF's alone SS_{APF}, EXMP at 2 K localized by the assist of APF's SS_{EXMP}, for cases (1) and (2). The first is shown by a dotted, the second by a solid, and the third by a dashed line. In (b), $SS_{EXMP}-SS_{APF}$ is shown as a function of x for cases (1) and (2), respectively. The experimental data (Refs. 1 and 13) are shown by ○.

$$\langle V_{APF}(\vec{r}_g)\rangle=\int V_{APF}(\vec{r}_g)|\phi_g(\vec{r}_g)|^2 d\vec{r}_g = -E_0(x)V_0\left(\frac{\nu_g^2}{(\bar{\sigma})^{-1}+\nu_g^2}\right)^{3/2}, \qquad (7)$$

where

$$\bar{\sigma}=\sigma\left(\frac{m}{m_e+m_h}\right)\times\left(\frac{E_H}{E_0(x)}\right).$$

Adding the APF energy of Eq. (7) to Eq. (2), we have the free energy for the EXMP localized by assist of APF's.

Now the primary interest is whether the EXMP assisted by APF's reproduces the SS observed in $Cd_{1-x}Mn_xTe$. First, the EXMP for $x=0.1$ calculated at 2 K is shown to be localized as in Fig. 2. Providing that the APF is not incorporated,

the exciton in this case is not localized, but extends throughout the crystal as implied by Fig. 1. The calculated SS, the energy difference between absorption and emission, is 9.1 meV, which is close to the experimental value 10.5 meV observed at 1.6 K for $Cd_{0.88}Mn_{0.12}Te$.[1,13] Next, the Mn concentration dependence of the SS together with the magnetic polaron energy is studied. For this aim, the Mn concentration dependences of both x_{eff} and Θ are required. We used an analytic x_{eff} given by Shapira *et al.*[23] and a numerical x_{eff} obtained with the simulation by Fatah *et al.*:[24] the former, referred to as case (1), agrees well with x_{eff} obtained from the experiment up to $x=0.1$,[23] while the latter, referred to as case (2), agrees well with x_{eff} up to $x=0.3$.[24] For Θ, the interpolated formula[3] for the experimental data[17] between $x=0.005$ and 0.3 was used. The calculated results at 2 K are shown in Fig. 3 for cases (1) and (2) together with the experimental data. The following characteristics are seen: (i) The SS for the EXMP (SS_{EXMP}) shown in Fig. 3(a) decreases drastically below $x=0.05$; this behavior seems consistent with the experiment by Golnik *et al.*[4] and Heiman *et al.*:[25] the L_2 line is observed clearly above $x=0.04-0.05$. The dotted line in Fig. 3(a) shows the SS for the exciton localized by APF's alone (SS_{APF}). (ii) The subtracted SS, $SS_{EXMP}-SS_{APF}$, at 2 K is shown in Fig. 3(b). This corresponds to the magnetic localization energy or the magnetic polaron energy obtained from the experiment.[1,12,13,26] We see the experimental data included are well correlated to the calculated result, although there remains the uncertainties in determining the polaron energies experimentally.[27] The Mn-concentration dependence of the magnetic polaron energy in the band-edge excitation is, thus, rather similar to the case of the ST-EXMP,[2,3] however is different from that obtained from the experiment in the selective excitation.[10] With increasing the temperature, the SS due to the magnetic localization becomes small and the exciton is almost localized by APF's. At a certain high-temperature range, the thermodynamic fluctuation of the magnetization becomes important, as similar to the case of BMP's.[5,6,8]

In conclusion, we investigated the effect of APF's on EXMP's after band-edge excitation theoretically within the MFA. The calculated results for the EXMP localized by the assist of APF's are consistent with experiments although the comparison was performed at relatively low temperatures. The present study thus strongly suggests the necessity of APF's to localization of EXMP's after band-edge excitation in bulk DMS's, e.g., $Cd_{1-x}Mn_xTe$, at least above $\sim$1 K.

[1] See, for example, S. Takeyama, in *Optical Properties of Low-Dimentional Materials*, edited by T. Ogawa and Y. Kanemitsu (World Scientific, Singapore, 1998), Vol. 2, Chap. 4.

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[27] From the time-resolved photoluminescence spectra, SS_{EXMP} is estimated from the energy shift at 300 ps, while SS_{APF} is obtained from the energy shift at 300 ps at high temperatures where the energy shift becomes insensitive to temperature. See Ref. 13 for more details.