Excitons in semimagnetic semiconductor quantum-well systems: Magnetic polaron effects

Ji-Wei Wu, A. V. Nurmikko, and J. J. Quinn
Brown University, Providence, Rhode Island 02912
(Received 10 February 1986)

The energy of the exciton formed from an electron and heavy hole in a narrow CdTe quantum well between barriers of $Cd_{1-x}Mn_xTe$ is evaluated using a simple variational trial function. The magnetic polaron effect, resulting from the exchange interaction of the carriers with localized Mn-ion spins located in the barrier, is included. Because of its heavier mass and small quantum-well depth, the hole is much more dramatically influenced by the magnetic polaron effect and tends to localize near one of the interfaces.

During the past two years it has become possible to fabricate high quality $CdTe/Cd_{1-x}Mn_xTe$ superlattices by molecular-beam epitaxy[1] (MBE). These novel semimagnetic semiconductor multiple-quantum-well (MQW) structures provide an excellent opportunity to study spin exchange interactions of quasi-two-dimensional carriers with the localized magnetic moments of the Mn ions in the $Cd_{1-x}Mn_xTe$ barrier layers. A number of experimental studies of the optical properties of such systems have been carried out recently.[2-6] For samples with low or moderate Mn concentrations in the barrier ($x<0.30$), where the antiferromagnetic coupling between Mn-ion magnetic moments is not strong enough to form spin-ordered states, the electronic properties in the quantum well are significantly affected by the existence of applied magnetic fields. Recent experimental evidence from photoluminescence suggests, among other things, that (heavy-hole) excitons formed in strained (111)-oriented structures are rather strongly localized at or near the $CdTe/Cd_{1-x}Mn_xTe$ heterointerfaces with an unexpectedly large amount of two-dimensional (2D) character. Furthermore, on applying an external magnetic field normal to the quantum-well layers a large spectral shift and a decrease of the exciton lifetime are observed. These effects appear to originate from the exchange interaction between the exciton and the Mn-ion spins. In $CdTe/Cd_{1-x}Mn_xTe$ quantum wells, the valence-band offset is known to be small, and it has been suggested that the origin of the exciton interface localization, even at zero magnetic field, contains a contribution from the spin exchange, i.e., a magnetic polaron effect.[2,3,7,8]

In a previous paper,[7] we calculated the ground-state energy of a heavy hole in the valence band of a single CdTe quantum well in a $Cd_{1-x}Mn_xTe$ host. The magnetic polaron effect was treated, within the mean-field approximation (MFA), as a nonlinear term in the single-particle effective Hamiltonian. Our self-consistent calculation shows explicitly that this nonlinear magnetic polaron term can appreciably reduce the effective potential in the region where the carrier is localized, so that for appropriate values of the applied magnetic field, the heavy-hole-like particle tends to localize near one of the interfaces. The calculated energy shift of the hole as a function of the external magnetic field agrees qualitatively with what can be deduced from the spectral shift of the exciton peak in photoluminescence experiments. However, such a single-particle calculation does not take into account the Coulomb interaction between the electron and hole, an essential ingredient in any study of exciton phenomena. A more meaningful comparison with the available experimental data for such a system would require a calculation of the quasi-two-dimensional exciton energy as a function of the applied magnetic field. Such a calculation is the objective of this paper.

The quasi-two-dimensional nature of excitons in such a system gives rise to anisotropic effects observed in experiments.[2,3] The large magnetic-field-induced spectral shift depends only on the field component normal to the interface. This is consistent with the fact that only the exciton spin component in that direction is a good quantum number. We use the exchange model involving only spin components normal to the interface and the result is independent of the field component parallel to the interface.

We present a variational calculation of the energy of the exciton[9-12] formed through the interaction of a conduction electron and a heavy valence-band hole in a CdTe quantum well. The light-hole energy levels lie much lower than that of the heavy hole because of the uniaxial strain in such a system. The mixing effect between the two types of holes are negligible. Very recently, Gonçalves da Silva[9] calculated energies of exciton states in heterostructure as a function of the hole position. His results, which detail the experimentally observed field anisotropy in terms of coupled heavy-hole–light-hole exciton states also, suggest a large penetration of the hole wave function into the barriers, and give qualitative agreement with the experiment. However, these calculations do not lead to a solution of the exciton ground state and cannot be compared directly with experiments. We start from a more realistic description, taking into account the effects of local potential fluctuations in forming an exciton magnetic polaron near the interface. Under this condition, we solve the exciton ground state from which an explicit description of a bound magnetic polaron can be deduced. In our model, the CdTe quantum well is contained in a semimagnetic $Cd_{1-x}Mn_xTe$ host, and the magnetic polaron effect is included in the exciton Hamiltonian through a nonlinear magnetic potential resulting

from the exchange interactions. Our mean-field approach gives excellent agreement with the line shift as a function of applied magnetic field observed in photoluminescence experiments.[2,3] Because of its relatively heavy mass and the small valence-band offset, the hole tends to form a magnetic polaron and localize near the well interface as a result of its exchange interaction with Mn ions inside the barrier. For the hole, this occurs even in the absence of an external field, while the electron in the conduction band remains confined near the center of the well even in the presence of a very large magnetic field. With increasing magnetic field, the hole moves further into the barrier resulting in a reduced overlap between the electron and hole wave functions. This effect causes appreciable variation in the expectation value of the electron-hole interaction. Although our results are based on a simple trial function, we believe that they correctly describe the physics underlying the problem.

The energy levels of excitons in a $CdTe/Cd_{1-x}Mn_xTe$ quantum well of width L are described by the following Hamiltonian involving the electron coordinate $\mathbf{r}_e$ and the hole coordinate $\mathbf{r}_h$:

$$H=\sum_{i=e,h}\left[[\mathbf{p}_i+(e/c)\mathbf{A}_i]^2/2m_i+V_i(z_i)-\alpha_i J_i^z\sum_n S_n^z\delta(\mathbf{r}_i-\mathbf{R}_n)\right]-e^2\epsilon^{-1}\,|\,\mathbf{r}_e-\mathbf{r}_h\,|^{-1}\,. \tag{1}$$

The first six terms describe the kinetic energy, quantum-well confinement potential, and the exchange interaction with the Mn ions for the electron and the hole. The last term describes the electron-hole Coulomb interaction. The background dielectric constant ϵ is taken to be the same in CdTe and $Cd_{1-x}Mn_xTe$. The single-particle barrier potentials are given by

$$V_e(z)=V_0^e\Theta(\,|\,z\,|-L/2)$$

and

$$V_h(z)=V_0^h\Theta(\,|\,z\,|-L/2)\,,$$

where $\Theta(z)=0$ for $z<0$ and is equal to unity for $z>0$. The sum

$$V_0^e+V_0^h=E_g(x)-E_g(0)\cong 1.5x\ \text{eV}$$

is equal to the band-gap discontinuity in a system with Mn-ion concentration x. We ignore the possible valence-band complexities and consider an orbitally nondegenerate heavy hole only. For the narrow wells which we consider ($L\approx a_B\approx 60$ Å, the exciton Bohr radius in bulk CdTe), the exciton is quasi-two-dimensional so that the spin-dependent Heisenberg-type interactions in Eq. (1) contain only the z components of relevant angular momenta. $J_e^z=\frac{1}{2}$ for an electron and $J_h^z=\frac{3}{2}$ for a heavy hole. The exchange constants α_e and α_h are taken to be those of bulk $Cd_{1-x}Mn_xTe$[3], although they may depend on the detailed forms of particle wave functions as well.[13] The orbital effect of the external field B_0 normal to the well is substantially smaller than the influence of the external field on the exchange interaction, and is entirely ignored in our calculation.

We adopt the same formal simplifications to the exchange terms in Eq. (1) as in Ref. 7. Averaging over the Mn-ion positions $\mathbf{R}_n$ inside the barrier, and taking the mean-field approximation for the Mn-ion spin polarization at a given temperature, allows us to write[7]

$$\sum_i S_i^z\delta(\mathbf{r}-\mathbf{R}_i)=\Theta(\,|\,z\,|-\tfrac{1}{2}L)N_0xS^z(\mathbf{r})\,,$$

where

$$S^z(\mathbf{r})=\tfrac{5}{2}\sigma(x)B_{5/2}(g_I\mu_B B_{\text{eff}}(\mathbf{r})/k_B(T+T_0))\,.$$

Here $B_{5/2}$ is the Brillouin function, g_I the Mn-ion g factor ($\frac{5}{2}$ that of an electron), and $\sigma(x)$ and $T_0(x)$ are parameters[13] describing approximately the antiferromagnetic interactions between isolated Mn-ions spins. The approximation used above is valid for systems with Mn-ion concentrations exceeding a few percent. The local effective magnetic field contributing to polarizing the Mn ion at position $\mathbf{r}$ is given by $B_{\text{eff}}(\mathbf{r})=B_0+B_x(\mathbf{r})$, where B_0 is the value of the external magnetic field and

$$g_I\mu_g B_x(\mathbf{r})=\alpha_e J_e^z\,|\,\psi_e(\mathbf{r})\,|^2+a_hJ_h^z\,|\,\psi_h(\mathbf{r})\,|^2 \tag{2}$$

is the exchange field acting on the Mn ion arising from the interaction with an electron in state $\psi_e(\mathbf{r})$ and a hole in $\psi_n(\mathbf{r})$. $B_x(\mathbf{r})$ gives finite contribution to the effective magnetic field only when the exciton is localized in space and spin polarizes the Mn ions in its neighborhood (i.e., the magnetic polaron effect).

Within the above simplifications and approximations, the orientational degrees of freedom of Mn ions in Eq. (1) are readily eliminated and the effective exciton Hamiltonian can be written as

$$H_{\text{eff}}=\sum_{i=e,h}\{p_i^2/2m_i+\Theta(\,|\,z_i\,|-\tfrac{1}{2}L)[V_0^i-V_m^iB_{5/2}(g_I\mu_B B_{\text{eff}}/k_BT_{\text{eff}})]\}-e^2\epsilon^{-1}\,|\,\mathbf{r}_e-\mathbf{r}_h\,|^{-1}\,. \tag{3}$$

Here we have introduced the amplitudes of the exchange potentials defined by

$$V_m^{e,h}\equiv\tfrac{5}{2}\sigma(x)xN_0a_{e,h}J_{e,h}^z$$

and have introduced $T_{eff}=T+T_0(x)$. Using parameters for $CdTe/Cd_{1-x}Mn_xTe$ quantum wells, we would generally have $V_0^e\gg V_m^e$ so that the electron is always confined near the well center even at very large magnetic fields. On the other hand, the condition $V_0^h<V_m^h$ is satisfied for the systems under consideration. The heavy hole may be attracted toward $Cd_{1-x}Mn_xTe$ barrier where the local effective field is large. The Schrödinger equation

$H_{\text{eff}}\bar{\Psi}=E\bar{\Psi}$ is nonlinear since the magnetic polaron term [Eq. (5)] depends on the eigenfunction. Our calculation shows that this magnetic polaron effect can lead to localization of the exciton near the interface even in the absence of an external magnetic field as suggested earler.[7]

To solve for the exciton energy we have performed a variational calculation on Eq. (3). The trial function is chosen to be of the form

$$\bar{\Psi}(\mathbf{r}_e,\mathbf{r}_h)=\psi_e(\mathbf{r}_e)\psi_h(\mathbf{r}_h)\ , \tag{4}$$

where

$$\psi(\mathbf{r})=\psi(\mathbf{r}_\perp,z)=\pi^{-1/2}\eta\exp(-\eta^2 r_\perp^2/2)\pi^{-1/4}\nu^{1/2}\times\exp[-\nu^2(z-z_0)^2/2]\ . \tag{5}$$

The parameters η, ν, and z_0 take different values for the electron and the hole, and each should carry a subscript e or h. In assuming the simple product function of Eqs. (7) and (8), we are ignoring the apparent separability of the degrees of freedom along the layer into center-of-mass and relative coordinates. We do this because we believe that the hole is localized in part by strains and fluctuations in the Mn-ion concentration, effects which break translational invariance along the layer. By using this trial function, we find for the expectation value of H_{eff},

$$E=\sum_{i=e,h}\left\{\hbar^2(\eta_i^2+\tfrac{1}{2}\nu_i^2)/2m_i+V_0^i[1-\tfrac{1}{2}\phi(\nu_i(\tfrac{1}{2}L-z_{0i}))-\tfrac{1}{2}\phi(\nu_i(\tfrac{1}{2}L+z_{0i}))]+\int d^3r_i\,\Theta(|z_i|-\tfrac{1}{2}L)V_m^i\,|\psi_i(\mathbf{r}_i)|^2 B_{5/2}(g_I\mu_B B_{\text{eff}}/k_B T_{\text{eff}})\right\}$$
$$-e^2\eta\epsilon^{-1}\int dz\exp[-\nu^2(z-z_0)^2+\eta^2z^2][1-\phi(\eta|z|)]\ . \tag{6}$$

In this equation

$$\eta=\eta_e\eta_h(\eta_e^2+\eta_h^2)^{-1/2}\ ,$$
$$\nu=\nu_e\nu_h(\nu_e^2+\nu_h^2)^{-1/2}\ ,$$

and

$$z_0=z_{0e}-z_{0h}\ .$$

The function $\phi(x)$ appearing in Eq. (6) is the error function defined by

$$\phi(x)=2\pi^{-1/2}\int_0^x dt\exp(-t^2)\ .$$

Although the variational wave function is of very simple Gaussian form, we believe it gives a reasonable estimate of the exciton energy. If this type of variational function is used in the absence of exchange interactions, the calculated exciton energy exhibits the expected behavior as a function of well width L. The error introduced by the approximation is probably smaller than that resulting from the uncertainty of material constants of the system.

Another question to address is whether the hole would tend to localize near both interfaces of the well, and whether this choice would have a lower exciton energy than the single-center wave function in Eq. (5). We have also calculated the exciton energy by using a generalized two-center hole wave function for comparison. In the small and medium field range, the magnetic polaron effect localizes the hole near one of the interfaces. In the large field limit, when the magnetization of the Mn ions has almost reached saturation, it is energetically more favorable for the hole wave function to be peaked near both interfaces. However, the exciton energy is lowered by a very small amount (<0.3 meV) compared to the single-center wave-function result. In real systems, the exciton localization is always associated with some local potential fluctuation near one of the interfaces, so a single-center hole wave function is more plausible.

With six possible variational parameters appearing in $\bar{\Psi}(\mathbf{r}_e,\mathbf{r}_h)$, the minimization of Eq. (6) could require a large computing effort. To simplify the numerical work we first fix the in-plane size of the heavy hole η_h^{-1} at a value of 15 Å as assumed in Ref. 7. This assumption is based on the fact that in real quantum wells there always exist local potential fluctuations within the extent of a few lattice constants.

Because of the deeper quantum well and weaker exchange interaction, the electron is not strongly influenced by the magnetic polaron effect. The parameters Z_{0e} and ν_e are found to vary little with magnetic field, always remaining close to their values in the absence of exchange interactions. These "empirical" observations allow us to simplify the computation without sacrificing accuracy.

As a specific example, we take the well width to be $L=60$ Å. For the effective masses we use $m_e=0.1m_0$ and $m_h=0.5m_0$, respectively. Other material parameters are taken for those of bulk $Cd_{1-x}Mn_xTe$ with $x=0.10$ from Ref. 13. This choice is reasonable even though typical samples used in photoluminescence measurements[2,3] have x values in the range of 0.20 in the barriers. The actual effective concentrations near the interface are difficult to evaluate experimentally, and we use the somewhat lower value also to account for finite gradients in the Mn-ion concentration. In the present case, the barrier heights are taken to be $V_0^e=126$ meV and $V_0^h=24$ meV, the latter predominantly due to strain splitting of the valence band. The exciton ground-state energy is now calculated by minimizing Eq. (6). For the parameter values given above, the magnetic field dependence of this energy is shown in Fig. 1. Up to moderate fields the exciton energy shifts quite linearly, while a saturation can be seen at

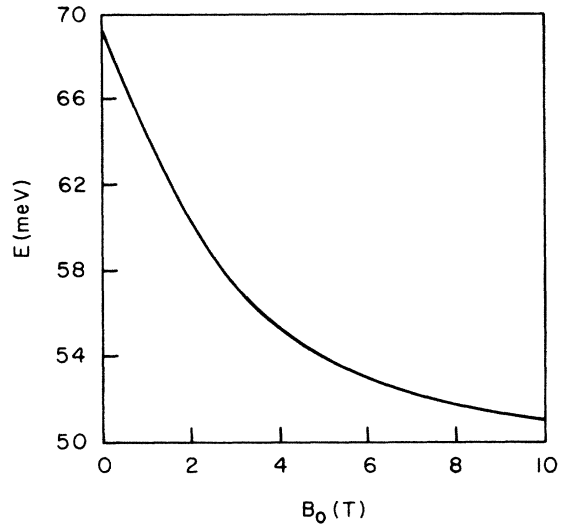

FIG. 1. Exciton energy (measured from the band gap of CdTe) versus the external magnetic field normal to the well. Parameters are either given in text or deduced from Ref. 13. $T+T_0=5$ K is used in the calculation.

large fields. The entire graph reproduces very well the spectral shifts observed in photoluminescence.[2,3] The total energy shift up to $B_0=10$ T is roughly 18 meV, which is quite close to the observed value. Given the uncertainty of sample parameters, this agreement is very good. It should be pointed out that there has been no accurate determination on the band offsets in such a system, although experimental measurements suggest that the valence-band offset should be generally less than 20%. Thus the choice of V_0^h is rather arbitrary to this extent. We carried out calculations for different values of V_0^h. We find that, although the calculated exciton energy depends on the specific value of V_0^h used in the calculation, the shape and magnitude of the exciton line shift as a function of the magnetic field are rather insensitive to choosing different values of V_0^h. The possible error arising from these uncertainties is comparable to the deviation of our results from the experimental observations in Ref. 2. In Fig. 2 we plot the center of the heavy hole z_{0h} for the same magnetic field range. In the absence of external fields ($B_0=0$), the hole is already located quite close to the interface ($L/2=30$ Å). This is entirely due to the magnetic polaron effect which gives rise to a nonzero B_x reducing the effective potential near the interface. On increasing the external field, the quantum-well confinement is reduced and the hole moves further into the barrier. Our calculation thus gives an explicit description of the interface localization of excitons proposed earlier. We find that in contrast to the hole, the electron is always located near the well center, a result due to the much higher barrier height in the conduction band. The electron-hole overlap is significantly reduced by applying a magnetic field. The relative displacement of the electron and the hole would induce a finite component to the exciton dipole moment in the z direction. This fact suggests that the system may now be more susceptible to optical excitations polarized normal to the well. The

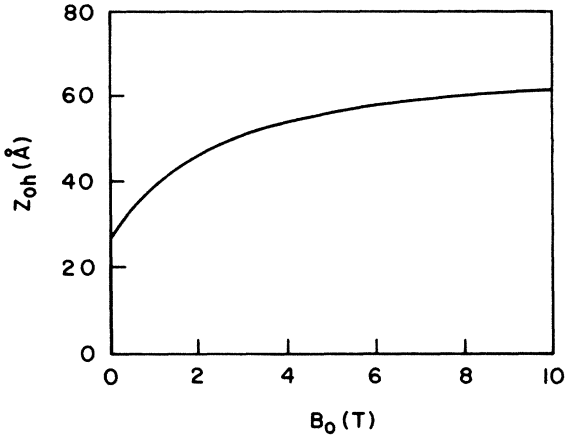

FIG. 2. Displacement of a heavy hole from the well center, in the same magnetic field range.

electron-hole Coulomb energy is shown in Fig. 3. This binding energy decreases on increasing the magnetic field, again a manifestation of the reduced overlap between the electron and the hole.

In summary, we have calculated the exciton energy in $CdTe/Cd_{1-x}Mn_xTe$ quantum-well structures. Our calculation provides the first direct comparison with the line shift observed in photoluminescence experiments. The newly discovered interface localization of excitons in such systems is quantitatively explained by the spin-exchange interaction with Mn ions in the barriers. These results should be useful in characterizing other semiconductor superlattice systems containing magnetic ions. We should also point out that the time evolution of excitons is ignored in our calculation. The observed exciton lifetime is comparable to the spin-relaxation time of Mn ions.[14] Further investigation is necessary for an understanding of the time-resolved spectra.

This work is supported by the U.S. Army Research Office and the U.S. Office of Naval Research. The authors acknowledge and thank Dr. C. E. T. Goncalves da Silva for sending us a report of his work (Ref. 9) prior to publication.

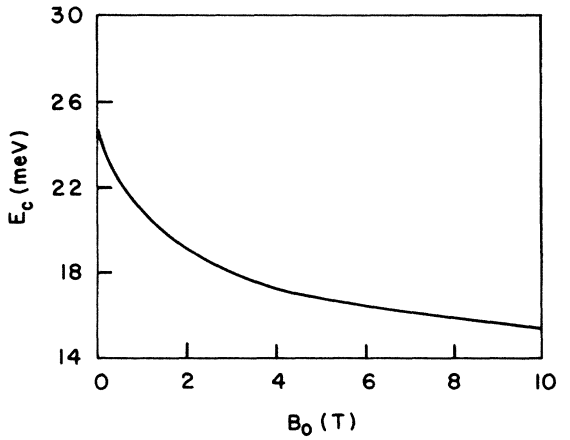

FIG. 3. The exciton Coulumb binding energy [the last term of Eq. (6)] versus the magnetic field.

[1]L. A. Kolodziejski, T. Sakamoto, R. L. Gunshor, and S. Datta, Appl. Phys. Lett. **44**, 700 (1984).
[2]X.-C. Zhang, S.-K. Chang, A. V. Nurmikko, L. A. Kolodziejski, R. L. Gunshor, and S. Datta, Phys. Rev. B **31**, 4056 (1985).
[3]X.-C. Zhang, S.-K. Chang, A. V. Nurmikko, D. Heiman, L. A. Kolodziejski, R. L. Gunshor, and S. Datta, Solid State Commun. **56**, 255 (1985).
[4]X.-C. Zhang, S.-K. Chang, A. V. Nurmikko, L. A. Kolodziejski, R. L. Gunshor, and S. Datta, Appl. Phys. Lett. **47**, 59 (1985).
[5]S.-K. Chang, A. V. Nurmikko, L. A. Kolodziejski, and R. L. Gunshor, Phys. Rev. B **33**, 2589 (1986).
[6]A. Petrou J. Warnock, R. N. Bicknell N. C. Gilles-Taylor, and J. F. Schetzina, Appl. Phys. Lett. **48**, 692 (1985).
[7]Ji-Wei Wu, A. V. Nurmikko, and J. J. Quinn, Solid State Commun. **57**, 853 (1986).
[8]C. E. T. Gonçalves da Silva, Phys. Rev. B **32**, 6962 (1985).
[9]C. E. T. Gonçalves da Silva, Phys. Rev. B **33**, 2923 (1986).
[10]R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981).
[11]G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **26**, 1974 (1982).
[12]R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 831 (1983); Phys. Rev. B **31**, 6498 (1985).
[13]J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).
[14]A. V. Nurmikko, X.-C. Zhang, S.-K. Chang, L. A. Kolodziejski, R. L. Gunshor, and S. Datta, Surf. Sci. (to be published).