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Excitons in diffused quantum wells

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The Schrödinger equation corresponding to the potential profile resulting from manganese diffusion in CdTe-$\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ quantum wells has been solved using a numerical method. Calculation of the exciton binding energies has allowed predictions of the effect of diffusion on the resulting optical properties of such quantum-well structures. In addition to the magnetic-field-dependent potential profiles that accompany the diffusion process, it is shown that the ratio of the Zeeman splitting of the light- and heavy-hole excitonic transitions is strongly dependent on the extent of the manganese diffusion. Consequently, this ratio can be used as a measure of the diffusion coefficient.

I. INTRODUCTION

Diffusion in semiconductor microstructures[1] has recently aroused increased general interest; for example Homewood and Dunston[2] and Nguyen Hong Ky *et al.*[3] and references therein. The importance of diffusion in the post growth fine tuning of devices is an important area of research,[4,5] as is the effect on the lifetime of devices, where diffusion during operation cannot be ignored. Attempts have been made to model the diffusion of dopants and constituent materials in various heterostructures, employing only approximate theories to predict the resultant effect on the optical properties. For example, the optical properties of quantum wells and superlattices are generally governed by exciton recombination; consequently in a complete theory it is not justifiable to ignore the excitonic effects.[6]

The aim of the present paper is to present complete calculations of the energies of excitons in diffused quantum wells. This facilitates meaningful discussion of the effect of diffusion on the optical properties, i.e., emission energies and oscillator strengths. The predictions made are general and applicable to any quantum-well system whether it be based on a III-V or II-VI material; however, the paper goes on to discuss the particular case of the diffusion of manganese, whose ions are magnetic. The magnetic properties of manganese Mn^{2+} ions give rise to novel potential profiles under the influence of an external magnetic field, which in turn leads to interesting excitonic effects.

II. THEORY

A. Exciton binding energies

A reliable model of a free exciton in a semiconductor crystal consists of treating it as an electron and a hole bound together via the Coloumb interaction. The problem for a quantum-well structure therefore becomes a two-body problem whose Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_h + \mathcal{H}_{\mathrm{eh}} \tag{1}$$

where $\mathcal{H}_e$ and $\mathcal{H}_h$ are the one-particle electron and hole Hamiltonians appropriate to motion along the z direction, whereas $\mathcal{H}_{\mathrm{eh}}$ represents the electron-hole interaction term and the kinetic energy of the relative motion in the xy plane

$$\mathcal{H}_{\mathrm{eh}} = \frac{p_\perp^2}{2\mu_\perp} - \frac{e^2}{\epsilon r}. \tag{2}$$

Here $p_\perp$ and $\mu_\perp$ are the momentum and reduced mass of the exciton perpendicular to the growth (z) direction, and the spatial separation r of the electron and hole is given by

$$r^2 = (x_e - x_h)^2 + (y_e - y_h)^2 + (z_e - z_h)^2. \tag{3}$$

The kinetic energy of the center-of-mass motion in the xy plane has been neglected since the ultimate interest lies in optical absorption and emission processes for which this energy must be zero by momentum conservation. The variational method used to solve the associated Schrödinger equation has been thoroughly described in the literature.[8–10] It is comprised of choosing a trial wave function Ψ, which is a product of three factors. (There is a fourth term corresponding to the product of the rapidly varying parts of the Bloch function of the electron and hole; however, these can be ignored for the present purpose since, within the envelope function approximation, their presence is manifested solely in the effective masses of the carriers.) The first two of these represent the uncorrelated one-particle electron and hole wave functions ψ_e and ψ_h, respectively, while the third is a term $\phi(r')$ representing the electron-hole interaction, i.e.,

$$\Psi = \psi_e(z_e)\psi_h(z_h)\phi(r'), \tag{4}$$

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where

$$\phi(r') = \exp\left(-\frac{r'}{\lambda}\right) \tag{5}$$

and

$$\begin{aligned} r'^2 &= (x_e - x_h)^2 + (y_e - y_h)^2 \\ &\quad +(1-\beta^2)(z_e - z_h)^2, \end{aligned} \tag{6}$$

with λ and β variational parameters.

The form of Ψ chosen above; in particular, the electron-hole interaction ϕ is a more general choice of wave function from that commonly found in the literature.[11–14] The inclusion of the parameter β allows the exciton to assume planar two-dimensional (2D), spherical (3D), or any intermediate symmetry should it be energetically favorable to do so. [In the calculation of exciton binding energies in type-II single quantum wells,[15] as indeed in superlattices,[9,10] where the electron and hole one-particle wave functions are spatially delocalized, the z dependence ($\beta^2 \neq 1$) of ϕ is essential to ensure localization (binding) of the total exciton wave function Ψ.]

Substitution of Ψ into Eq. (1) leads to an equation for the total energy of the system

$$E = E_e + E_h - E_b, \tag{7}$$

where E_e and E_h are the electron and hole one-particle energies, i.e.,

$$E_e = \frac{\langle\psi_e|\mathcal{H}_e|\psi_e\rangle}{\langle\psi_e|\psi_e\rangle}, \tag{8}$$

and correspondingly for the hole. The exciton binding energy E_b is given by

$$\begin{aligned} -E_b = \frac{\hbar^2}{2\mu} \frac{\int |\psi_e|^2|\psi_h|^2|\frac{\partial\phi}{\partial z_e}|^2 \; d\tau}{\int |\psi_e|^2|\psi_h|^2|\phi|^2 \; d\tau} \\ +\frac{\int |\psi_e|^2|\psi_h|^2(\phi\mathcal{H}_{eh}\phi) \; d\tau}{\int |\psi_e|^2|\psi_h|^2|\phi|^2 \; d\tau}. \end{aligned} \tag{9}$$

The formalism developed so far is independent of the specific form of the (uncorrelated) one-particle electron and hole wave functions ψ_e and ψ_h. In particular, it can therefore be applied to any semiconductor heterostructure whose one-particle Schrödinger equations are solvable. In the present paper the shooting technique of Killingbeck[7] was used to determine the one-particle energies E_e and E_h as well as the uncorrelated envelope functions ψ_e and ψ_h for the electron and hole, respectively, in a diffused quantum well.

Comparison with systems having analytical solutions, e.g., single finite quantum wells and Pöschl-Teller potential holes, indicates that this numerical method yields accurate one-particle energies (to within 0.001 meV). The envelope functions obtained give exciton binding energies that also agree to within 0.001 meV.

The variational calculation is implemented by adjusting the parameters λ and β until the exciton binding energy is maximized, thus minimizing the total energy of the system.

B. Diffusion

Diffusion has been investigated since the early 19th century. Fick expressed the time and direction dependence of diffusing substances in two equations, known as Fick's first law,

$$F = -D \,\mathrm{grad}\, c, \tag{10}$$

and Fick's second law

$$\frac{\partial c}{\partial t} = \mathrm{div}\, D\, (\mathrm{grad}\, c)\,. \tag{11}$$

In Cartesian coordinates Eq. (10) gives in one dimension

$$F = -D\frac{\partial c}{\partial z}, \tag{12}$$

while Eq. (11) gives

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} D\left(\frac{\partial c}{\partial z}\right), \tag{13}$$

which includes the time dependence of the diffusion process.

Various standard solutions to the linear case of Fick's second law do exist,[16,17] depending on the initial distribution of the diffusing substance. For the following calculations Crank's[16] solution to the diffusion equation for a source with an initial distribution that is a step function has been employed. Using c_0 for the initial concentration of the diffusing substance, Crank's equation reads

$$c = \frac{c_0}{2}\,\mathrm{erfc}\,\frac{z}{2\sqrt{Dt}}, \tag{14}$$

where erfc denotes the complementary error function. The supposed linearity of Fick's second law, i.e., the constancy of the diffusion coefficient D, now allows a linear superposition of the separate solutions to the diffusion equations.

The model employed below is based on the following assumptions:

(1) No diffusion takes place during the growth of the quantum-well structure. Instead, all the diffusion is assumed to occur while the sample is being annealed. There are two reasons for making this assumption. First, since the structures are only a few hundred angstroms wide, the growth time of the considered samples is only a tiny fraction of the total annealing time . Second, the annealing temperature is normally significantly higher than the growth temperature, thus resulting in a much lower diffusion coefficient during the growth of the sample.

(2) Only one substance is actually diffusing.

It should also be pointed out that the following calculations are not microscopic in the sense that there is no reference to impurity atoms or lattice defects, such as interstitials or vacancies (which can enhance diffusion processes dramatically). For such a calculation, which takes impurities and lattice defects into account, a diffusion Monte-Carlo analysis would be necessary. However, the macroscopic model employed is of proven utility for abstracting information from experimental data.[9]

Figure 1 shows diffusion profiles for a single well of width 80 Å, surrounded by $Cd_{0.925}Mn_{0.075}Te$ barriers. As a linear diffusion process has been assumed, the curves are universal, i.e., the diffusion coefficient and the time are interchangeable. Hence the separate graphs are labeled with the corresponding product of diffusion coefficient D and time t. For example, if we assume for the graph with the largest amount of diffusion a diffusion coefficient of $D = 0.1$ Å^2/s, we obtain, by using the Dt value of 5×10^3 Å^2, a corresponding annealing time of $t = 50000$ s ≈ 14 h.

As CdTe:$Cd_{1-x}Mn_xTe$ structures are grown in the author's laboratory the diffusion profile can be applied to obtain the concentration distribution resulting from the diffusion of Mn^{2+} ions from the barriers into the quantum well. Since the band gap is proportional to the concentration of Mn^{2+}, the distribution of these ions represents directly the potential shape of the conduction and valence band at zero field.

C. Effect of magnetic field on diffused magnetic wells

When one of the constituents of a quantum-well system is a magnetic ion, such as manganese in the $Cd_{1-x}Mn_xTe$ barrier surrounding a CdTe well, there exists the opportunity for some novel effects on the application of an external magnetic field. The reason is that the band gap of the dilute magnetic semiconductor $Cd_{1-x}Mn_xTe$ can be either increased or decreased with respect to CdTe, depending on whether the optical transitions associated with σ^- or σ^+ polarizations respectively, are observed.[18] The conduction-band edge of $Cd_{1-x}Mn_xTe$ changes by an amount $3A$, and the heavy-hole valence band by an amount $3B$, where

$$|A| = \frac{1}{6} x N_0 \alpha s_0(x) B_J(\mathbf{B}, x, T) \tag{15}$$

and

$$|B| = \frac{1}{6} x N_0 \beta s_0(x) B_J(\mathbf{B}, x, T), \tag{16}$$

where $N_0\alpha$ and $N_0\beta$ are constants equal to 220 and 880 meV, respectively. The parameter $s_0(x)$ is the effective spin of the manganese ions; it accounts for the antiferromagnetic coupling between the ions, and is a function of x. $B_J(\mathbf{B}, x, T)$ is a modified Brillouin function that depends upon the external magnetic field $\mathbf{B}$, the manganese concentration x, and the temperature T.

The σ^- polarization observes an increase in the apparent band gap of $|3A| + |3B|$, and the σ^+ polarization observes a decrease in the band gap of $|3A| + |3B|$. The changes in the conduction-band potential $3A$ and the valence-band potential $3B$ of a given alloy concentration x are nonlinear functions of the magnetic field, and this, coupled with the variation in alloy composition due to diffusion as depicted in Fig. 1, produces highly nonlinear field-dependent conduction- and valence-band responses. This is illustrated in Fig. 2. The graph shows the effect of an external magnetic field on the valence-band potential of a 74-Å CdTe well surrounded by $Cd_{0.925}Mn_{0.075}Te$ barriers (assuming a 35% valence-band offset) after an amount of diffusion characterized by $Dt = 50$ Å^2.

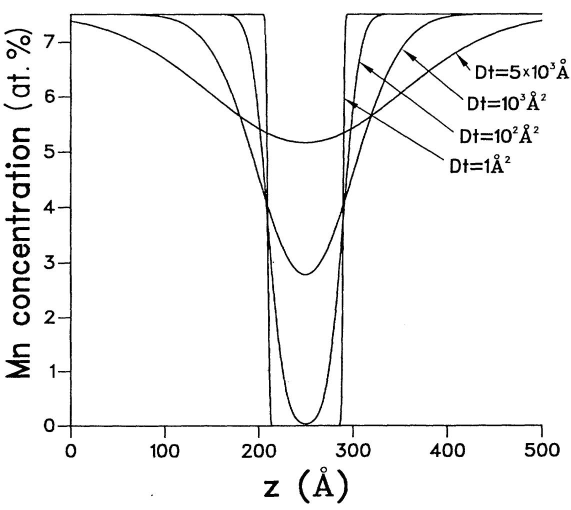

FIG. 1. Diffusion profiles for manganese diffusion in an 80-Å CdTe well surrounded by $Cd_{0.925}Mn_{0.075}Te$ barriers.

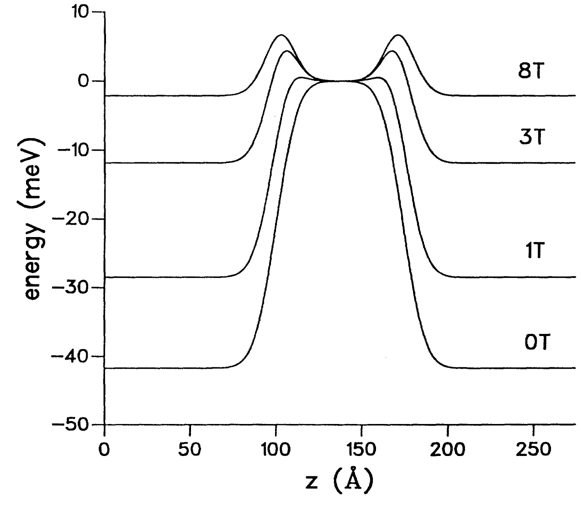

FIG. 2. Effect of magnetic field on $m_J = -\frac{3}{2}$ valence-band potential profile of a 74-Å CdTe quantum well surrounded by $Cd_{0.925}Mn_{0.075}Te$ barriers after 50 Å^2 of diffusion.

III. RESULTS AND DISCUSSION

Figure 3 shows the zero-field ground-state electron wave function for the 80-Å diffused well corresponding to the value of $Dt=10^3$ Å^2, as in Fig. 1.

Figures 4–6 summarize the effect of manganese diffusion on the excitonic properties of quantum wells of width 20, 50, 80, and 110 Å. In all three graphs the diffusion constant was taken to be 0.1 Å^{2}s^{-1}. Hence the independent variable becomes the annealing time t and not the product Dt. The effect of a different diffusion constant D can be obtained by rescaling the time t axis. Note that 40% of the total offset was taken to lie in the valence band in all calculations. Although different offsets may change the particular exciton energies, the qualitative forms of all curves are the same and hence any conclusions drawn from them are completely general.

The change in the exciton emission energies as a function of time is displayed in Fig. 4. As can be seen, the effect of diffusion is to increase the photoluminescence emission energy. This is in agreement with observations made by Elman *et al.*,[19] who measured vacancy-enhanced Ga/Al interdiffusion at the heterojunction between GaAs single quantum wells and the surrounding $Al_xGa_{1-x}As$ barriers. The exciton emission energy shifts of the quantum wells (QW2 and QW3) of Elman *et al.* have diffused to such an extent that they are showing signs of saturating. Further annealing of these quantum wells will produce saturation when the well material begins to assume the same constituency as the barrier, as depicted in Fig. 4 presented here.

Figure 5 shows that the enhancement in the emission energy, after a certain annealing time, is a nonmonotonic function of well width; this is also in agreement with experimental measurements of Elman *et al.*[19]

The relative (rel.) oscillator strengths for the 20-, 50-, and 80-Å wells are displayed in Fig. 6. The overall result of diffusion at these three well widths is an increase in the oscillator strengths, although the rate of the increase is different for each well (indeed, for the widest of the wells the eventual increase is preceded by a slight decrease).

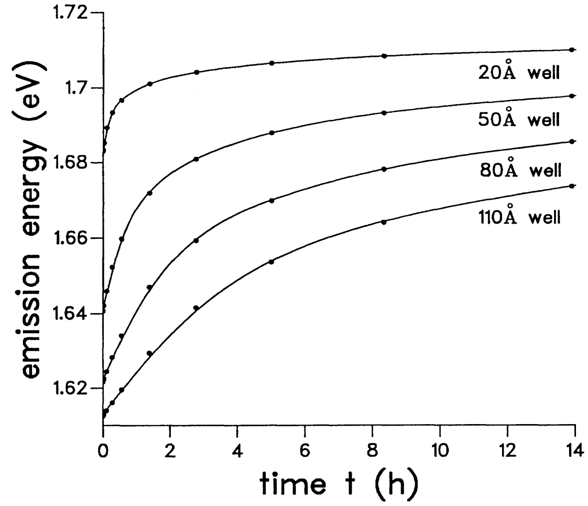

FIG. 4. Effect of diffusion on the exciton emission energy of CdTe quantum wells, as a function of time t for the diffusion constant $D=0.1$ Å^2 s^{-1}.

The results presented in Figures 4, 5, and 6 can be readily explained in terms of the effect of diffusion on the well width and the relative positions of the (uncorrelated) one-electron and -hole energy states with respect to the bottom of the well.

Examination of the diffusion profiles in Fig. 1 indicate that at the onset of diffusion the manganese close to the interface with the CdTe is able to move immediately into the well. This has the effect of raising the potential in the well and reducing the potential in the barrier adja-

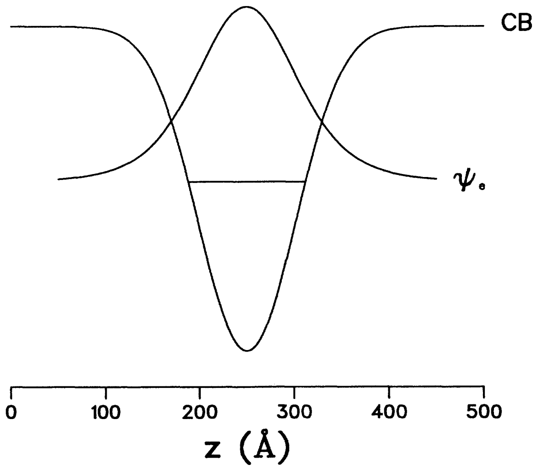

FIG. 3. Diffusion profile of an 80-Å well with $Dt=10^3$ Å^2 and the corresponding electron wave function produced with the shooting technique.

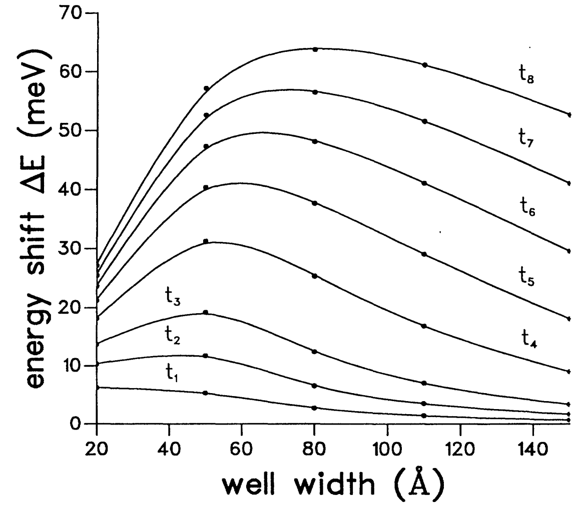

FIG. 5. Enhancement of the exciton emission energy due to manganese diffusion as a function of time t for the diffusion constant $D=0.1$ Å^2 s^{-1}. The quoted times t_1, t_2, etc., in order are 400, 1000, 2000, 5000, 10 000, 18 000, 30 000, and 50 000 s.

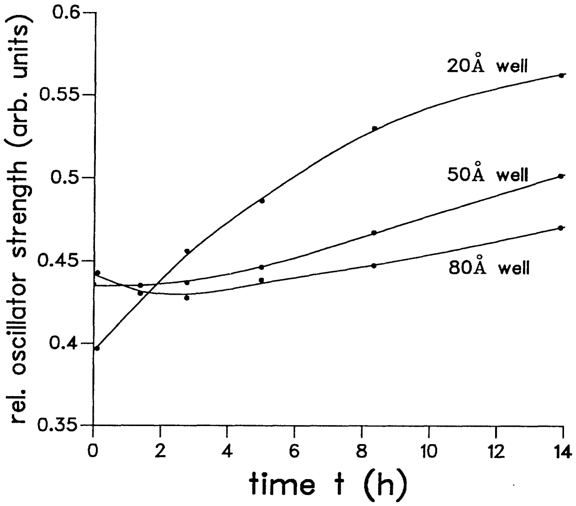

FIG. 6. Relative (rel.) oscillator strength as a function of time t for the diffusion constant D=0.1 Å^2 s^{-1}.

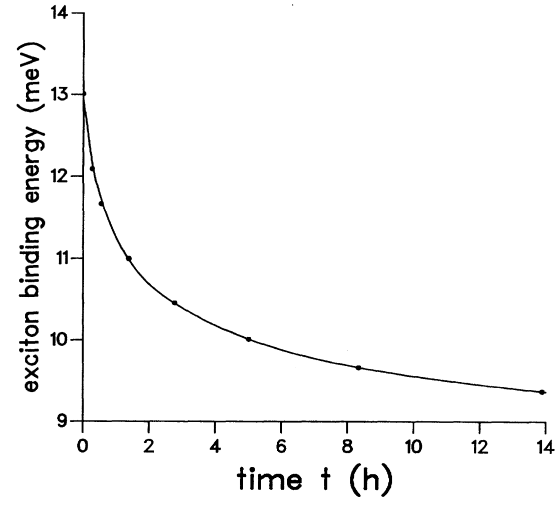

FIG. 7. Exciton binding energies for the 20-Å well as a function of time t, for the diffusion constant D=0.1 Å^2 s^{-1}.

cent to the interface. Hence on an energy scale the well appears to narrow at lower energies and widen at higher energies. However, manganese eventually diffuses into the center of the well, turning it into a dilute form of the barrier alloy. Hence the potential at the center of the well is increased. This has the effect of increasing the apparent band gap. An important property of the CdTe/Cd$_{1-x}$Mn$_x$Te system is the 6:1 ratio of the effective mass of the heavy hole to that of the electron. This has the effect of a lower confinement energy and hence a higher degree of localization for the hole, compared to the electron.

Initially in the narrow 20-Å well the electron penetrates deeply into the barriers surrounding the square well, whereas the heavier hole sits much lower in the well with a higher degree of confinement. As diffusion occurs the electron "sees" a well widening and hence the confinement energy of the electron decreases and its localization increases. Conversely, the hole "sees" a well narrowing, hence its confinement energy increases and its localization decreases. This has the effect of increasing the overlap integral, and hence the oscillator strength rises, as in Fig. 6. However, as the exciton binding energy is more strongly dependent upon the degree of localization of both particles and not just their overlap, then the decreasing localization of the hole dominates over the increasing localization of the electron. The counterintuitive result is a reduction in the exciton binding energy (as in Fig. 7) at the same time as an increase in the oscillator strength. The increase in the confinement energy of the hole together with the decreasing binding energy and the increasing apparent band-gap result in the increasing exciton emission energy as in Fig. 4.

For the wider wells the electron and hole have lower one-particle energies. At the onset of diffusion they observe a slightly narrower well, and this, together with the increase in the apparent band gap, leads to an increase in their uncorrelated energies. Therefore the exciton emission energy increases too, as is shown in Fig. 4. The increasing confinement energies also produce greater delocalization; hence a reduction in the exciton binding energies occur (similar to Fig. 7) and an initial decrease in the oscillator strengths occur. As diffusion proceeds further; then, although the electron and hole continue to delocalize, their overlap increases slightly, leading to the slight rise in oscillator strengths, as in Fig. 6.

Figure 8 shows the effect of the diffusion (measured in terms of the product of the diffusion coefficient with time) on the σ^+-σ^- Zeeman splitting of the heavy-hole (HH) and light-hole (LH) excitonic well transitions of the diffused quantum well of Fig. 2. It is immediately apparent that the Zeeman splitting of the heavy-hole exciton energy levels can be enhanced dramatically from

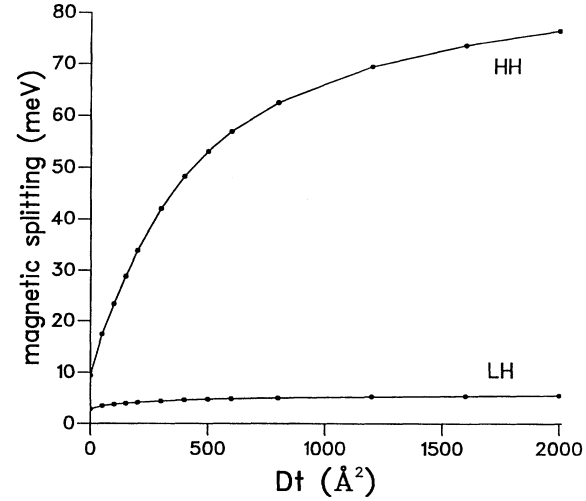

FIG. 8. Effect of diffusion on heavy-hole (HH) and light-hole (LH) σ^+-σ^- Zeeman splittings at 8 T of quantum well corresponding to Fig. 2.

the quantum well, with abrupt interfaces. This is due to the presence of magnetic ions in the well, which directly effect the well energy levels, rather than indirectly, as in the case were they appear only in barriers. The negligible effect on the light-hole can be understood in terms of the reduction in the quantum confinement effects compared with the heavy hole, coupled with the much reduced Zeeman splitting of the light-hole states (one-third that of the heavy hole). Figure 8 displays an opportunity to experimentally measure the amount of diffusion in a magnetic system, as the ratio of the heavy-to light-hole splitting is a sensitive function of Dt. As the annealing time t is easily measured, this allows for the determination of the diffusion coefficient D.

IV. CONCLUSION

The effect of diffusion on the exciton emission energies has been found to be in agreement with experiment. In particular, the calculations show that the photoluminescence emission energy increases with greater annealing and that the resulting shift is a nonmonotonic function of well width.

Diffusion of a magnetic ion from the barriers into a quantum well (in this case Mn^{2+}) has been shown to produce novel potential profiles and enhance the magnetic-field Zeeman splitting of the heavy-hole absorption lines. It has been argued that the ratio of the heavy- to light-hole magnetic-field splittings could be used to determine the amount of diffusion that has occurred and hence the diffusion coefficient.

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