Band offsets and excitons in CdTe/(Cd,Mn)Te quantum wells

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The question of band offsets and details of exciton binding are investigated in the CdTe/(Cd,Mn)Te heterostructure in the quantum-well limit. Photoluminescence excitation spectroscopy in external magnetic fields is used to vary the quantum-well potential depths in this moderately strained (0.6% lattice mismatch) diluted magnetic semiconductor heterostructure. Large Zeeman splittings are observed at all the principal quantum-well transitions and at the barrier band gap for a structure of CdTe well thicknesses of 50 Å and a Mn-ion concentration in the barrier layer of $x=0.24$. A variational theory is developed for excitons, especially accounting for the possibility of a small valence-band offset. Good agreement between theory and experiment is obtained and a band offset of 25 meV is deduced for the heavy-hole valence band, corresponding to a conduction- to valence-band offset ratio of about 14:1. This implies that the valence-band offset in a hypothetical strain-free case is virtually zero. The accuracy of the offset determination is believed to be better than 10 meV. Exciton binding energies are found to vary appreciably in the magnetic field; the zero-field value is approximately twice that for bulk CdTe.

I. INTRODUCTION

The CdTe/(Cd,Mn)Te superlattice system is a relatively new example of a II-VI compound semiconductor heterostructure which is suitable for growth by molecular beam epitaxy (MBE).[1] Such epitaxy permits growth in either [111] or [001] orientation on GaAs substrates.[2] While a number of early optical investigations have implied that the valence-band offset in this superlattice is quite small,[3] accurate quantitative determination of this and related fundamental quantities has remained incomplete. As a motivation, a case of nearly zero band offset is an interesting one for study from two points of view. First, there is considerable contemporary interest in the question of band offsets in semiconductor heterostructures and quantitative connections between various experimental techniques and predictions by theoretical models. Second, insofar as exciton effects are strong in wide gap II-VI compound semiconductors, the details of the Coulomb binding are particularly intriguing in a situation of a nearly two-dimensional (2D) electron and a quasi-3D hole.

In this paper we present experimental measurements and related theory, the purpose of which is to extract band offset parameters and exciton binding energies for the CdTe/(Cd,Mn)Te system in the quantum-well limit. We exploit the large magneto-optical effects present in diluted magnetic semiconductors (DMS) such as (Cd,Mn)Te to measure Zeeman splittings of the lowest quantum-well exciton transitions in an external field through photoluminescence excitation spectroscopy, these splittings originating from induced changes in the effective electron and hole potential wells. The ability to magnetically "tune" the quantum-well potentials is of key importance in providing a varied experimental data base for calculations. The experiments focus on the behavior for the $n=1$ heavy-hole (HH) and $n=2$ HH excitons for which variational calculations are then applied. We find indeed that the valence-band offset for the heavy-hole state in a simple rectangular potential-well model is practically zero when corrected for the built-in strain in the structure. However, in order to bring theory and experiment into agreement, it is critical to include properly the excitonic effects which add to the net potential well for the hole due to the electron Coulomb interaction. Below, we develop a variational approach which is particularly suitable in treating the exciton problem in a quantum well where one of the quasiparticles is subject to weak confinement. The final band offset determination is believed to be accurate to better than 10 meV; this makes the optical methods employed here and their interpretation attractive when compared, e.g., with photoemission techniques.

The organization of this paper is as follows. Experimental details and results are described in Sec. II. Theory of excitons in DMS quantum wells in external magnetic fields is developed in Sec. III for the CdTe/(Cd,Mn)Te heterostructure and compared with experiment. This yields both band offset and exciton binding information. The implications are discussed and summarized in Sec. IV.

II. EXPERIMENTAL RESULTS

In this work we focus on a particular CdTe/(Cd,Mn)Te multiple quantum-well (MQW) structure, grown in [001] orientation. Strain-related effects in the [111]-oriented structures are apparently responsible for significant broadening of the ground-state exciton resonances[4] so that precise spectroscopic determination of transition energies is difficult. The sample grown by MBE methods on a GaAs (001) substrate is reported previously,[2] starting with a buffer-layer structure consisting of approximately 1.87 μm (Cd,Mn)Te with Mn concentration $x=0.24$ on a 0.57-μm-thick layer of CdTe. The MQW portion of the structure contained 30 periods of CdTe and (Cd,Mn)Te of $x=0.24$, with a layer-thickness ratio of approximately (50 Å)/(82 Å). The choice of the particular Mn concentration was made by considering both the need to obtain a substantial band-gap difference but yet to keep lattice mismatch strains moderate in the heterostructure. For unstrained bulk CdTe, the low-temperature (excitonic) band gap is at 1.596 eV and that for the alloy ($x=0.24$) is approximately 382 meV larger (see below for direct experimental determination of the latter in the MQW structure). A 0.6% lattice-constant mismatch is elastically accommodated with a moderate dislocation density and leads to finite strain adjustments to the band gaps for the CdTe "wells" and (Cd,Mn)Te "barriers." Uniaxial strain is the dominant factor in removing the heavy- and light-hole valence-band degeneracy (loss of cubic symmetry).

The layer thicknesses in the MQW structure were obtained from measurements by high-resolution transmission electron microscopy (TEM) which is subject to an approximate error of less than 5 Å; below, we will use the mean value for the effective CdTe well thickness of 50 Å as it also best matches the theory with experiment. The TEM images also showed the presence of sharp, defect-free interfaces.[5] Photoluminescence excitation spectroscopy was performed in backscattering geometry with a low-power tunable dye laser ($P\sim 1$ mW) loosely focused on the samples. The samples were inserted into a superconducting magnet Dewar and immersed in liquid helium. The results reported here are qualitatively very similar to those obtained in another MQW sample with an 84-Å well thickness.

Figure 1 shows the excitation spectrum for the MQW sample at $T=2$ K in zero field over the energy range of interest, as probed at the dominant recombination exciton transition. The principal low-energy features in the figure are the $n=1$ HH and LH (light hole) excitons, labeled as E_{1H} and E_{1L}, respectively (in this notation, the effective masses are referred to the z direction of the superlattice axis). The LH exciton transition is considerably broadened, presumably by its large penetration into the (Cd,Mn)Te barrier. We also observed some additional sharp structure in the $n=1$ exciton region, evidently due to exciton-LO phonon coupling. This detail is not included in Fig. 1 and will not be discussed further in this paper. Such structure has been recently studied by Viña and co-workers in [111]-oriented CdTe/(Cd,Mn)Te quantum wells at considerably lower levels of Mn concentration than those considered here.[6] In addition, the excitation spectra at higher photon energies display the transition for the $n=2$ HH exciton at 1.925 eV (E_{2H}) and that for the (Cd,Mn)Te alloy barrier at 1.990 eV (E_{BH}). The $n=2$ LH transition was not resolved for this particular sample. Both of the higher-energy peaks are broadened, most likely also due to alloy compositional fluctuations in the barrier within the exciton Bohr radius. The measurement of the actual barrier band gap in the strained structure is important since it can be directly used as input in quantum-well calculations to be described below. Comparing the value obtained here with data on bulk (Cd,Mn)Te we find that this corresponds to a Mn concentration $x=0.245$ in bulk and is, in fact, within the uncertainty of the absolute calibration of concentration by electron microprobe and optical measurements on separate thin alloy films. However, the gap measured in the MQW sample also includes the effects of hydrostatic and uniaxial lattice mismatch strains.

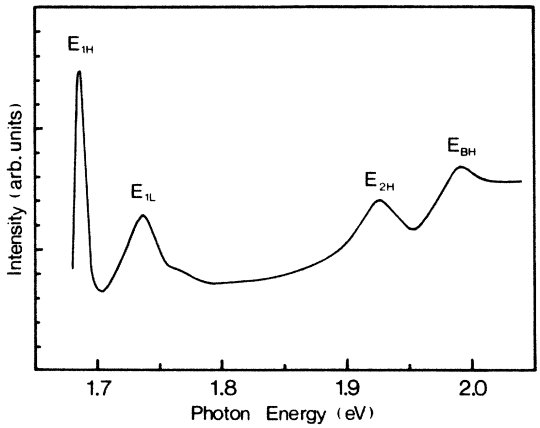

FIG. 1. Luminescence excitation spectrum for a [001]-oriented CdTe/(Cd,Mn)Te MQW sample ($L=50$ Å) at $T=2$ K, showing the $n=1$ HH and LH, $n=2$ HH, and the barrier band-gap excitonic resonances.

The influence of an external magnetic field is to split all of the observed optical transitions. Figure 2(a) displays the $n=1$ HH and LH region in the zero field for reference and Fig. 2(b) highlights the large splitting of the $n=1$ HH exciton ($\Delta E=13$ meV) for the field in the direction of the superlattice axis ($B_z=4$ T). This corresponds also to the Faraday configuration and well-defined circular polarization selection rules are obeyed, as indicated in the figure (which is actually a superposition of two excitation spectra obtained for opposite circular polarizations). In contrast, the LH exciton shows much weaker changes in this field geometry; however, as shown in Fig. 2(c) with the field oriented in the layer plane, rather large splitting of the LH exciton was observed, approximately 17 meV in $B_x=4$ T. In this geometry the HH splitting was reduced to less than 4 meV. The source for such field anisotropy will be briefly discussed in Sec. IV. In addition to the $n=1$ HH Zeeman splittings, both the $n=2$ HH and the ground-state exciton at the barrier band gap exhibited large splittings with the anticipated circular polarization selection rule

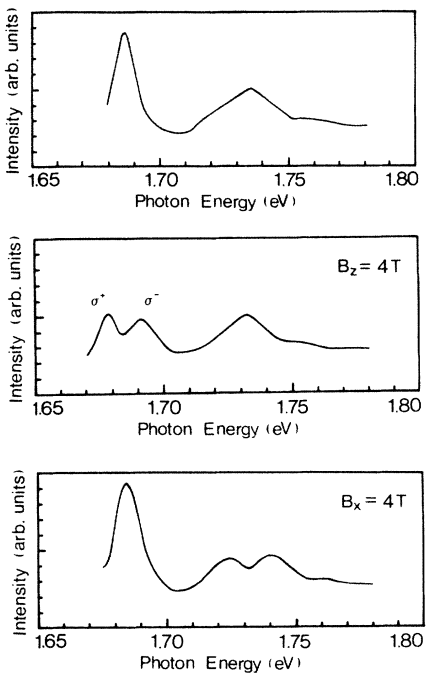

FIG. 2. Excitation spectra for the $n=1$ HH and LH exciton in zero field (top), in 4-T field parallel to superlattice axis (middle), and in 4-T field perpendicular to superlattice axis (bottom).

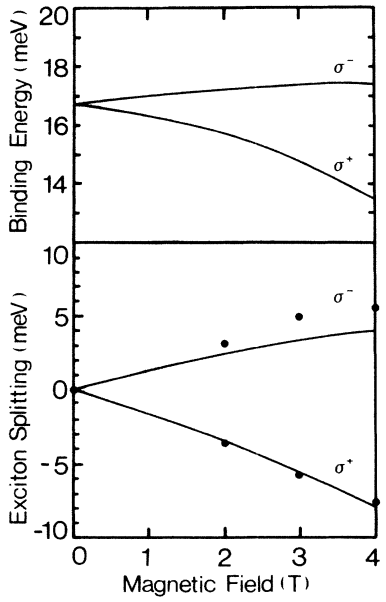

FIG. 3. Comparison of experiment (dots) and theory (with a 25-meV valence-band offset) for the Zeeman splitting of the $n=1$ HH exciton (lower panel), and the field-induced changes in the exciton binding energy (upper panel).

being obeyed in Faraday geometry. Specifically, in a field of $B_z=4$ T, the splitting for the former was $\Delta E=44$ meV and for the latter $\Delta E=79$ meV. The measurement of the Zeeman splitting at the barrier band gap was important in calibrating the observed magneto-optical effects at the quantum-well transitions as discussed below.

A summary of the $n=1$ HH exciton splitting is shown in Fig. 3 for several values of the applied field (lower panel). The figure also includes results of our calculations (solid lines) with specific band offset values and exciton binding energies (upper panel) as detailed in Sec. III. The splitting into lower- and higher-energy components was found to be somewhat asymmetrical for both $n=1$ and 2 HH excitons (with respect to the zero-field energy position) in the sense that the shift of the lower-energy component always exceeded that of the high-energy one. This provides an important additional clue for characterizing the valence-band offset and the exciton in this quantum-well system.

III. THEORY AND CALCULATIONS

The presence of the transition-metal ion Mn in a II-VI semiconductor host such as CdTe is known to lead to large magneto-optical effects at the fundamental gap at low temperature as a consequence of the exchange interaction of the spins of extended Bloch band-edge states with those of the Mn-ion d electrons. In a quantum well or a superlattice, the occurrence of corresponding "giant" Zeeman effects can be readily exploited to characterize the electronic details of the structure, in particular, to obtain information about the degree of electron and hole confinement and excitonic interactions. In this section we first review briefly the main features of DMS materials and then develop a theory for excitons in a DMS quantum well for interpretation of the experimental measurements described above. The theory takes special note of the complication encountered here, namely, that the valence-band offset is comparable to or may be even smaller than the electron-hole Coulomb interaction in the structure. In the usual variational approach to excitons in quantum-well structures, the trial function in the envelope-function approximation is initially factored into a product of one-particle envelope functions of the electron and the hole and a wave function for the electron-hole relative motion.[7–9] In our case, such a theory becomes less accurate since it assumes that the one-particle envelope functions are solutions to the simple quantum-well potential without explicit modification by the Coulomb interaction.

In the elementary one-electron and hole picture, Fig. 4 depicts the influence of an applied magnetic field on a CdTe/(Cd,Mn)Te quantum well, assuming a rectangular well potential in the condition and valence bands. We emphasize here the role of the heavy-hole valence states while noting that the light-hole states are initially split from these at Γ point due to the uniaxial component of the lattice mismatch strain in both the CdTe well and (Cd,Mn)Te barrier layers (signs of strain are opposite). The effect of the applied field is to alter the quantum-well potential heights due to the spin splittings in the (Cd,Mn)Te barrier layers so that different effective potential barriers exist for the various spin split electron and hole components. We assume throughout this paper that the exchange effects dominate over Landau quanti-

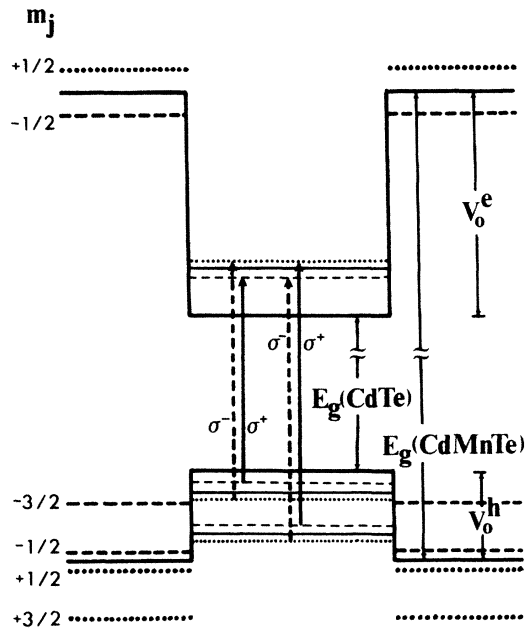

FIG. 4. Schematic of the influence of the external field on the quantum well in electron-hole representation.

zation and neglect the latter. Circularly polarized optical transition in Faraday geometry for the lowest interband $|\frac{3}{2},\pm\frac{3}{2}\rangle$ to $|\frac{1}{2},\pm\frac{1}{2}\rangle$ transitions are also indicated in the figure. These selection rules were already illustrated in the experimental results of Fig. 2(b).

The spin splittings at the barrier band gap can be immediately written down by using a well-established formulation of the problem in DMS bulk materials. In the barrier layer of (Cd,Mn)Te, the HH valence and conduction band splittings can be written as

$$V_m^e(B_z)=\mp\tfrac{1}{2}N_0\alpha x\langle S_z\rangle\ ,$$
$$V_m^h(B_z)=\pm\tfrac{1}{2}N_0\beta x\langle S_z\rangle\ , \tag{1}$$

where N_0 is the total cation density, x the Mn-ion alloy fraction, α and β the conduction electron and valence hole exchange coefficients, and $\langle S_z\rangle$ the thermodynamical average of the ion spin in the direction of the applied field. This formulation also gives direct and useful insight for the CdTe/(Cd,Mn)Te quantum-well problem since any spectral shifts and splittings measured for the confined particle transitions can be compared with values obtained in bulk (Cd,Mn)Te to get a measure of the degree of electron-hole wave-function penetration into the "exchange active" (Cd,Mn)Te barrier.[10] For a Mn-ion concentration such as $x=0.24$, appropriate corrections must be made for the antiferromagnetic interaction among the Mn-ion spins which acts to reduce the effective spin splittings. Empirically, the influence of the antiferromagnetic (AF) Mn-Mn spin coupling is often accounted for by writing a modification into the Brillouin function $B_{5/2}$ (Ref. 11) to reflect changes in paramagnetic behavior as

$$\langle S_z\rangle=S_0B_{5/2}[\tfrac{5}{2}g\mu_BB_z/k_B(T+T_0)]\ , \tag{2}$$

where $S_0\leq\frac{5}{2}$ and $T_0\geq 0$ are concentration-dependent correction factors.[11] However, at a Mn-ion concentration as high as that encountered here this formulation becomes questionable as an *a priori* means to calculate the field-induced changes at the barrier band gap. As already noted, we have circumvented the problem by directly measuring the Zeeman shifts ΔE at the barrier layer band-gap resonance for the superlattices under investigation. One assumption we do make in this paper concerning the magnetic behavior is to ignore any complications which might arise from the presence of the heterointerfaces. This is a difficult subject matter in the sense that specific microscopic details on the scale of the chemical bond lengths may influence the AF interactions for spins within about a monolayer (~ 3 Å) from the interface.[12] The point of view we take here is that for the *absorbing* exciton which is measured through excitation spectroscopy, the quantum-well electronic states are of long enough wavelength so that the interface regions encompass only a small fraction of the total exciton wavefunction penetration into the (Cd,Mn)Te barrier.

With this approach to the magnetic interactions, we write the exciton Hamiltonian in the effective mass approximation for a single rectangular CdTe/(Cd,Mn)Te quantum well as follows:[13]

$$\begin{aligned}H_{\rm eff}&=\sum_{i=e,h}\{p_{zi}^2/2m_i+\Theta(|z_i|-\tfrac{1}{2}L_z)[V_0^i\pm V_m^i(B_z)]\}\\&\quad+\frac{p_\perp^2}{2\mu}-e^2/\epsilon[r_\perp^2(+z_e-z_h)^2]\\&\equiv h_e(z_e)+h_h(z_h)+p_\perp^2/2\mu-e^2/\epsilon[r_\perp^2+(z_e-z_h)^2]\ ,\end{aligned} \tag{3}$$

where

$$h_e(z_e)\equiv p_{ze}^2/2m_e+[V_0^e+V_m^e(B_z)]\Theta(|z_e|-L_z/2)$$

and similarly for $h_h(z_h)$. The zero-field potential-well depths are V_0^e and V_0^h in the conduction and valence bands, modified to yield a set of spin split quantum wells in the external field by $V_m^e(B_z)$ and $V_m^h(B_z)$. We assume that uniaxial component of the lattice mismatch strain and confinement effects have removed the heavy- and light-hole degeneracy of the valence bands so that Eq. (3) can be applied to these states separately. At the same time we ignore in this paper the heavy- and light-hole coupling induced by the superlattice potential or strain; such complications will be investigated separately in later work. Thus, the quantities V_0^i include the effects of the lattice mismatch strain; their contribution is discussed in Sec. IV. The width of the quantum well is L_z and the Θ function is a step function with the origin $z=0$ at the center of the well. The "magnetic" term in Eq. (3) is written in this particular form partly for schematic reasons; as noted above, we put into our calculations the directly measured values for field-induced changes in the (Cd,Mn)Te barrier layer band gap at a given field and temperature so as to eliminate possible ambiguities of this description. The momentum opera-

tor in the quantum-well layer plane is $p_\perp$, the reduced electron-hole mass is μ, and the electron-hole Coulomb interaction appears as the last term in the Hamiltonian (3), screened by a dielectric constant ϵ.

We obtain the solution to the exciton Hamiltonian in Eq. (3) by using a variational approach[7] with a trial wave function of the form

$$\psi(r_\perp,z_e,z_h)=\psi_e(z_e)\psi_h(z_h)\phi_{e-h}(r_\perp,z_e-z_h)\ , \tag{4}$$

where ψ_e and ψ_h are the electron and hole one-particle confined wave functions in the z direction and $\phi_{e-h}(r_\perp,z_e-z_h)$ is the wave function for relative electron-hole motion. Because of the Coulomb nature of the electron-hole interaction, ϕ_{e-h} can be taken to be of the form of a hydrogen atom wave function either in 3D space[8] or confined to the 2D plane of a quantum well[9] with similar results. In particular, we choose

$$\phi_{e-h}(r_\perp,z_e-z_h)=\phi_{e-h}(r_\perp)$$
$$=(2/\pi)^{1/2}\lambda^{-1}\exp(-r_\perp/\lambda)\ , \tag{5}$$

with λ as a variational parameter. The total interband energy as measured in the experiment is

$$E_T=E_g'+E_e+E_h-E_b\ , \tag{6}$$

where E_g' is the band gap of the CdTe well including the effect of the hydrostatic (compressive) component of the lattice mismatch strain. We estimate this contribution to increase the CdTe band gap by 11 meV by assuming a free-standing superlattice and using the elastic constants of CdTe throughout the structure. The confinement energies and the exciton binding energy E_b are expressed as

$$\begin{aligned}
&E_e=\int dz_e\psi_e^*(z_e)h_e(z_e)\psi_e(z_e)\ ,\\
&E_h=\int dz_h\psi_h^*(z_h)h_h(z_h)\psi_h(z_h)\ ,\\
&-E_b=\hbar^2/2\mu\lambda^2-e^2\epsilon^{-1}\int dz_e\,|\psi_e(z_e)|^2\int dz_h\,|\psi_h(z_h)|^2\int d^2r\,|\phi_{e-h}(r_\perp)|^2/[r_\perp^2+(z_e-z_h)^2]\ .
\end{aligned} \tag{7a}$$

We simplify the expression for the exciton binding energy by developing the last term in Eq. 7(a) into the following form:[14]

$$-E_b=\hbar^2/2\mu\lambda^2-e^2(\epsilon\pi)^{-1}\int_{-\infty}^{\infty}dQ\int dz_e e^{iQz_e}|\psi_e(z_e)|^2\int dz_h e^{-iQz_h}|\psi_h(z_h)|^2\int d^2r_\perp|\phi_{e-h}(r_\perp)|^2K_0(r_\perp Q)\ , \tag{7b}$$

where K_0 is the modified Bessel function. In the second term on the right-hand side, all three internal integrals over z_e, z_h, and $r_\perp$ can be expressed by elementary functions, so that E_b can eventually be evaluated by numerically integrating over the wave vector Q introduced above. This algebraic step reduces the computing effort substantially, without sacrificing accuracy.

In the overall calculation we must keep in mind that, unlike the case, e.g., with the (Ga,Al)As quantum wells, the situation here is likely to involve only a small offset in the valence band. Consequently, the one-particle functions $\psi_e(z_e)$ and $\psi_h(z_h)$ can no longer be assumed to be simple solutions of $h_e(z_e)$ and $h_h(z_h)$ in Eq. (3) due to the presence of the large exciton Coulomb perturbation. Specifically, whereas the electron is tightly confined in the CdTe layers, the Coulomb potential acting on the hole significantly modifies its effective potential in the z direction. In the variational approach used by us, and described in detail elsewhere,[15] the total interband exciton energy is obtained by assuming that ψ_e and ψ_h correspond to the presence of "effective quantum wells" of depths V_e and V_h, respectively, which self-consistently include the Coulomb interaction. These quantities V_e and V_h together with λ are the full set of variational parameters which are obtained for a particular value of the external magnetic field. These effective wells thus contain the z component of the Coulomb interaction so that in the final solution $V_e>V_0^e+V_m^e(B_z)$ and $V_h>V_0^h+V_m^h(B_z)$ as expected. When comparing with experiment, the calculation is put to a rather stringent test as the magnetic fields employed in our experiments substantially modify the valence-band effective potential-well depth. As mentioned above, the band gap of the (Cd,Mn)Te and its spin splitting (heavy-hole components) were directly obtained from experiments on the same quantum-well sample; the separate contributions to conduction- and valence-band exchange potentials were taken to have a ratio of 1 to 4, based on measurements in bulk (Cd,Mn)Te, where $N_0\alpha=220$ meV and $N_0\beta=880$ meV.[11] For the relative electron and hole effective masses, we took $m_e=0.096$ and $m_h^z=0.4$ for the z direction. In the x-y layer plane we used $m_h^{xy}=0.15$. While the valence-band parameters for CdTe are not entirely accurately known, the z-directed masses reflect available experimental data;[16] for the perpendicular masses we employed Lawaetz's considerations.[17] Since the effective masses in (Cd,Mn)Te are not known, we employed CdTe masses throughout; the actual corrections to our final results should be small. Finally, $\epsilon=9.7$ for CdTe was used.

Figure 5 shows results of calculations for the $n=1$ HH exciton transition used by us in part to determine the valence-band offset V_0^h. The zero-field and Zeeman splitting of the interband transition (at $B_z=4$ T) are

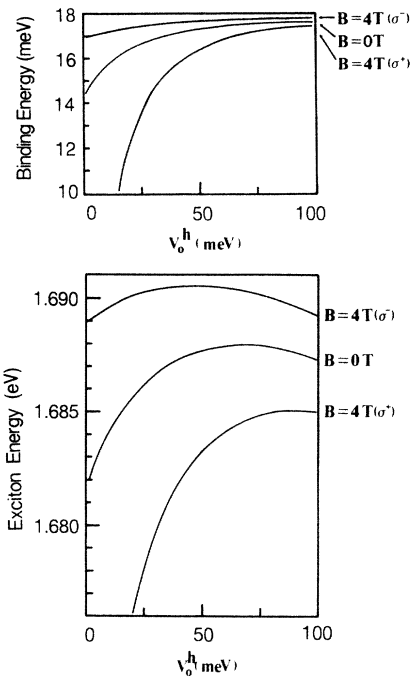

FIG. 5. Interband exciton energy as a function of the valence-band offset in zero and 4 T field (lower panel), and variations in the exciton binding energy (upper panel). A "best" offset of 25 meV is extracted.

graphed as a function of the offset (lower panel), where a V_0^h in the range of 20–30 meV matches quite well with the interband energies and the experimentally observed splitting. Variation in the exciton binding energy is also shown (top panel) for the same range of band offsets. The figure displays the distinct asymmetry in the magnitude of the Zeeman shifts for the σ^+ and σ^- components (referenced to the zero-field transition energy); this asymmetry is, however, considerably less than estimated in the electron-hole picture and reflects the key role of Coulomb forces in a situation where one of the spin split HH components possesses a very small V_0^h (i.e., a nearly type-II quantum well). For this range of V_0^h values the agreement for the Zeeman splitting of the $n=2$ HH transition is also quite good, as are the predicted zero-field positions for both the $n=1$ and $n=2$ HH transitions. The calculation based on the $n=2$ experimental data yields, however, a slightly larger effective offset; this is in part due to decreased accuracy in the variational approach as the hole for this transition is nearly unbound. By taking the "best" $V_0^h=25$ meV and keeping all the variational parameters fixed, Fig. 3 compares the theory with experiment for the Zeeman splitting of the $n=1$ HH exciton as a function of the magnetic field. The good agreement serves as an important demonstration of the consistency of our calculations for this transition. For the MQW structure in question, the conduction band offset is thus approximately 360 meV, reflecting a band offset ratio of about 14 to 1. Changes in the exciton binding energy in the external magnetic field were also naturally obtained from the calculations, and the upper panel of Fig. 3 shows E_b for the lowest spin split $n=1$ HH component. The situation for the $n=1$ LH exciton is more ambiguous as the large Zeeman splittings were obtained in a geometry where the direction of the magnetic field was perpendicular to the superlattice axis [Fig. 2(c)]. This makes analysis of the data more complicated since the $|m_j|$ can no longer be used as good quantum numbers. The origin of the large field anisotropy for the LH exciton (as well as the HH exciton) is, however, qualitatively clear, reflecting the combined action of the superlattice potential (quasi-2D hole) and uniaxial strains on the valence-band states. Similar large field anisotropies have been previously encountered in bulk (Cd,Mn)Se, a DMS wurtzite structure where crystal field effects split the valence-band degeneracy at $k=0$ and lead to hexagonal (uniaxial) symmetry.[18] We have made rough calculations about the band offset for the light hole in the CdTe/(Cd,Mn)Te system and, while lacking the accuracy of the heavy-hole case, find that it is noticeably smaller than that for the HH particle. Similar to the case of the $n=2$ HH transition, the variational approach is subject to a larger uncertainty in this instance as the hole is nearly unbound.

IV. DISCUSSION AND SUMMARY OF RESULTS

The experimental and theoretical results detailed above yield band offset information for the CdTe/(Cd,Mn)Te MQW system at a lattice temperature of $T=2$ K which we believe is accurate to better than 10 meV. However, in order to reach such precision, we have found that proper accounting of the exciton contribution to the interband transition energies is critically important. Some of the details of the variational calculation were discussed in Sec. III, and we note again that the circumstances of a small V_0^h pose special problems for proper handling of the Hamiltonian equation (3). Compared with the results from previous approaches by other authors,[7–9] the methods employed here yield significantly lower ground-state interband energy for heterostructures with a small valence-band offset. The Coulomb interaction provides, so to speak, additional confinement for the hole, and indeed plays a key role in preventing the superlattice from becoming type II (as would be predicted, for example, in the electron-hole picture for the highest fields considered here up to 4 T). The exciton binding energies for the $n=1$ HH transition are influenced by the external field while remaining well above the value $E_b \sim 9$ meV for bulk CdTe (Fig. 3). Nonetheless, the weak hole confinement prevents E_b from reaching those large enhancements expected for a fully 2D exciton.

The question of band offsets in semiconductor heterojunctions has been discussed recently from different experimental and theoretical viewpoints with some debate as to the degree of precision and reliability involved in each particular method. The experiment and theory described here for the CdTe/(Cd,Mn)Te heterostructure, with emphasis on the magnetically tunable $n=1$ HH exciton, makes a strong case for an offset in the valence band of this quantum-well system which is less than

10% from that occurring in the conduction band. For this conclusion, we have further experimental support also from recent measurements by resonant Raman spectroscopy involving the interaction of excitons with longitudinal optical phonons in this particular structure.[19] The value of $V_0^h = 25$ meV for the $|m_j| = \frac{3}{2}$ valence band was obtained above by putting the variational theory to a rigorous test in a quantum-well system where the band offsets are significantly altered by the applied magnetic field. While the offset values thus obtained refer to a system where a moderate strain is present, we can also make a crude extrapolation into the strain-free limit by accounting for the uniaxial component of the lattice mismatch strain in the conventional way (the question of the role of the hydrostatic component in determining band lineups is subject to a considerable uncertainty as its accurate evaluation would imply precise knowledge about the absolute conduction- and valence-band energies of the entire system). For the [001] strain, the HH-LH splitting at $k = 0$ is estimated to be -25.4 meV in the CdTe layers and approximately $+13.6$ meV in the (Cd,Mn)Te layers assuming a free-standing superlattice. In the estimate we use the following elastic constants for CdTe and (Cd,Mn)Te of $x = 0.24$, respectively: $C_{11} = 5.36$, $C_{12} = 3.70$, $C_{11} = 5.195$, and $C_{12} = 3.593$.[20] The relevant deformation potential constant was taken as $b = 1.2$.[21] Assuming that there is no mixing of the $|m_j| = \frac{3}{2}$ and $|m_j| = \frac{1}{2}$ states, we thus obtain that in the "strain-free" limit of the [001] CdTe/(Cd,Mn)Te heterojunction the net effective band offset V_0^h for the HH valence band in the square-well model considered here is practically zero, and certainly less than 10 meV. A similar conclusion is also reached for the LH band which may even yield a slightly type-II superlattice in the presence of the strain. We note that our results are also compatible with earlier measurements by Pessa and Jylhä[22] in somewhat different circumstances, who used photoemission techniques to indicate a small band offset for a [111]-oriented CdTe/(Cd,Mn)Te heterointerface grown by atomic layer epitaxy.

Among the theories which have recently addressed the band offset question in semiconductor heterojunctions, there is some agreement that the so-called common anion rule has very little real basis for a general validity. For example, Tersoff[23] has presented results for a number of II-VI compound semiconductors and argued that a small valence-band offset in a common anion system is quite unlikely and, if occurring at all, reflects some fortuitous coincidence. Experimentally, however, there are rather few measurements available for II-VI systems to date, and comparisons between experiment and theory have been mainly discussed in connection with the HgTe/CdTe superlattice where early experimental indicators of a relatively small valence-band offset[24] have been challenged by later experiment and theory.[23,25] In another case of the CdTe/ZnTe superlattice,[26] a very large lattice mismatch strain ($\sim 7\%$) complicates the epitaxial growth and experimental interpretation of optical spectra (as well as theory), but there are indirect indicators which suggest that the operative valence-band offset is also rather small.[27]

In the present case of the CdTe/(Cd,Mn)Te heterostructure, the strains are rather moderate and only affect the band offsets on the scale of about 20 meV as estimated above. A question can thus be raised as to the physical origin for such a small V_0^h in this system. The concentration of the Mn ion in the alloy barrier chosen here ($x = 0.24$) was sufficiently high so that a fairly large electronic "contrast" is present at the heterojunction ($\Delta E_g \sim 400$ meV). There are recent photoemission measurements on bulk (Cd,Mn)Te alloys, including work by Taniguchi *et al.*[28] and Spicer and co-workers[29] which show that the position of the valence-band maximum (VBM) is unaffected by the addition of Mn into CdTe up to $x \simeq 0.60$ within the accuracy of the experiment (presumably not better than some 50 meV). Some hybridization of the Mn-ion d-electron states with the valence p states does, of course, occur but, as these authors show, this has little influence on the VBM position at $k = 0$. One may, therefore, speculate that the experimental observation of a nearly zero band offset in the CdTe/(Cd,Mn)Te heterojunction implies the lack of any significant dipole effects at the heterointerfaces on the electronic states in question, perhaps reflecting dielectric similarities between Cd and Mn. We note that if we compare our experimental results with the prediction by Tersoff for a zinc-blende CdTe/MnTe junction,[23] a sizable discrepancy appears as the theory implies a much larger valence-band offset than observed. On the other hand, we are not aware of specific predictions for this material system among the alternative recent theoretical approaches (such as those based on *ab initio* pseudopotentials),[30] but clearly future comparison would be of interest.

The calculations presented in this paper have used the assumption of a simple rectangular potential energy profile in the superlattice and explicitly ignored the mixing of heavy- and light-hole valence-band states. Obviously, such mixing should be considered in a more sophisticated theory, particularly insofar as it might yield states, e.g., at the heterointerfaces in the case of small valence-band offsets. [For the recombining exciton, trapping at CdTe/(Cd,Mn)Te interfaces has been demonstrated, particularly for the [111]-oriented structures.[31]] The case of an inherently small V_0^h is also susceptible for other perturbations (e.g., of impurity charges) which may distort the potential-energy profiles across the shallow heterojunction. If such contributions play a role, it is conceivable that different experimental techniques such as interband optical spectroscopy at the fundamental gap and photoemission techniques may in fact measure different effective band offsets since a very different range of k space is involved in the two cases.

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