Polaronic excitons in $Zn_xCd_{1-x}Se/ZnSe$ quantum wells

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Magneto-optical absorption of quantum wells exhibits distinct excitonic resonances and allows the determination of exciton binding energies and diamagnetic shifts. Here, we report a magneto-absorption study on $Zn_{0.69}Cd_{0.31}Se/ZnSe$ multiple quantum wells 4 and 5 nm thick yielding $1S$ exciton binding-energy values. These results are compared to calculations based on two theoretical models that include the exciton-phonon interaction potential or the screened Coulomb potential. This analysis allows us to discriminate between the two models and highlights for the first time the impact of polaronic coupling on the optical behavior of these polar heterostructures.

In recent years wide-gap II-VI semiconductor heterostructures have attracted much attention mostly in light of their potential for the development of opto-electronic devices operating in the blue-green spectral region.[1] Owing to their relatively large exciton binding energies (E_b), they also offer the possibility of realizing quantum wells (QW's) in which excitonic recombination is dominant even at room temperature.[2] These systems, however, also present other unique properties such as strong exciton-phonon interactions (from here on referred to as polaronic effects) which make them ideal candidates for the investigation of the impact of these effects on the optical spectra.

Polaronic effects have been extensively studied in the past,[3,4] and significant polaron-related modifications of fundamental optical properties were demonstrated in bulk ionic semiconductors. Much less attention, on the contrary, was paid to this issue in systems with reduced dimensionality, e.g., QW's. In fact in the experimental analyses of excitonic effects in II-VI QW's,[5–8] the role of polarons in determining the exciton binding energies was not adequately addressed, and was actually often overlooked. This was probably due to a large body of studies focused on GaAs-based heterostructures[9,10] where polaronic effects are indeed negligible owing to the low-ionicity of the atomic bonds.

In this report, we address this issue by analyzing the magneto-absorption properties of $Zn_xCd_{1-x}Se/ZnSe$ QW's. Our results demonstrate the important role played by polaronic effects in determining excitonic optical properties. We shall show that by including polaronic effects using an effective potential first derived by Aldrich and Bajaj[3] it is possible to reproduce quantitatively our experimental results within an envelope-function formalism with no adjustable material parameters.

Samples studied were grown by solid source molecular-beam epitaxy on GaAs(001) substrates. They consist of a 0.5-μm GaAs buffer layer grown at 580°C followed by 1.5 μm-thick ZnSe layer grown at 290 °C. Ten $Zn_{0.69}Cd_{0.31}Se/ZnSe$ QW's were then grown at 250 °C with a 30-s interruption at each interface. A 500 nm-thick cap layer concluded the growth. ZnSe barrier width is 30 nm; 4 and 5 nm-thick QW's were examined. In order to detect transmission signals, circular regions of about 6×10^{-4} cm^2 were selectively removed using standard photolitographic and wet-etching techniques. Owing to the high- Cd concentration in the well, the energy separation between $1S$ heavy- and light-hole excitons is much enhanced by the compressive strain in the QW's (it is larger than 50 meV). This condition makes it possible to resolve the absorption associated to the continuum edges, even at zero-magnetic field. It should be noted that despite the large Cd content the $1S$ heavy-hole exciton absorption peak at $T=1.6$ K displays a full width at half maximum of about 9 meV indicating good sample quality. This was also confirmed by the small Stokes shift of the photoluminescence signal (≈1 meV). Samples were mounted on a variable-temperature insert and magnetic fields B between 0 and 10 T were applied parallel to the growth direction. Magneto-absorption was studied using a 100 W Xenon lamp as source. Light was focused and collected along the growth direction by optical fibers. Transmitted intensity was carefully normalized to the incident light in order to detect absorption changes.

Figure 1(a) shows typical spectra at $T=1.6$ K for the sample with QW thickness $L_w=5$ nm at zero-magnetic field and with an applied magnetic field of 10 T. The two peaks at 2528 meV and 2610 meV observed in the $B=0$ spectrum are associated to the $1S$ (hh1-e1) heavy- and (lh1-e1) light-hole exciton, respectively, as confirmed by linear polarization-dependent absorption measurements. Additional structure is observed at around 2560 meV. Thanks to the high-confinement potential, one further higher-energy peak due to the $1S$ (hh2-e2) heavy-hole exciton[11] is also observed.

Upon application of the magnetic field, the $1S$ heavy- and light-hole exciton peaks display a small blueshift and no appreciable oscillator strength enhancement. This behavior is

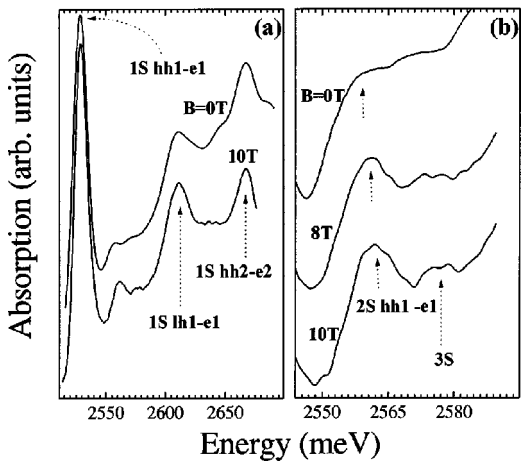

FIG. 1. (a): Absorption spectra for the $Zn_{0.69}Cd_{0.31}Se/ZnSe$ sample with 5 nm well width at magnetic fields $B=0$ T and $B=10$ T. The magnetic fields are applied along the growth direction (Faraday configuration). (b): Magnification of the absorption spectra in the heavy-hole continuum edge region at three different magnetic fields.

immediately understood in light of their large binding energy in comparison to the cyclotron energy ($E_c=5.2$ meV at 10 T). The light-hole exciton, however, displays a peculiar nonmonotonic behavior, which may be linked to valence-band mixing effects.[7] The heavy-hole continuum edge (energy region around 2560 meV), on the contrary, is dramatically altered, and a sharp peak on its low-energy side gradually emerges with increasing magnetic fields [see Fig. 1(b) where absorption spectra in the region of the continuum edge are displayed at three different magnetic fields]. This feature can be unambiguously associated to the heavy-hole $2S$ excitonic level because of its diamagnetic behavior in the range $6\ \text{T} \leqslant B \leqslant 10$ T (see Fig. 2). The diamagnetic shift of that level ($\delta E \approx 4$ meV) indicates that the Coulomb interaction is still significant in the investigated range of magnetic fields. A further peak, visible from 8.5 T is identified with the $3S$ excitonic level. In this magnetic field range, however, this exciton state acquires a Landau-like magnetic-field dependence that, contrary to the $2S$ exciton case, indicates the predominance of the free-carrier cyclotron energy E_c over the exciton binding energy. This behavior is in agreement with the theory developed in Ref. 12.

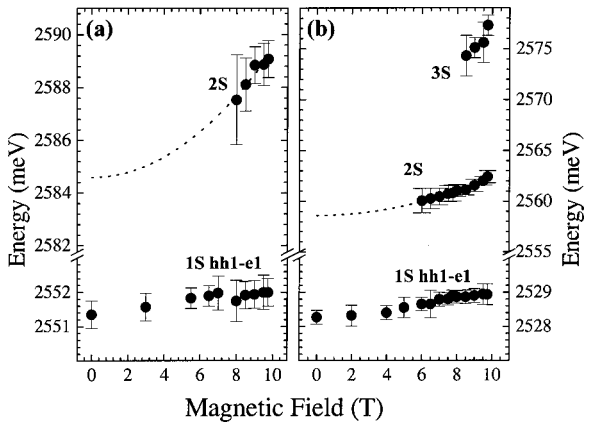

FIG. 2. Energy of $1S$, $2S$, and $3S$ hh1-e1 exciton absorption peaks as a function of magnetic field for both the 4 nm width sample (a) and 5 nm width sample (b). Dashed lines are a quadratic fit to the experimental points for $2S$ excitons. The quadratic coefficients for the fit are 0.048 meV/T^2 (a) and 0.037 meV/T^2 (b).

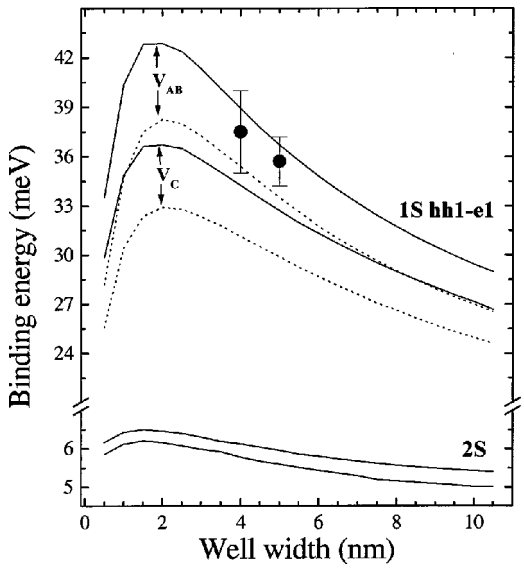

FIG. 3. Upper part: Calculated values of $1S$ hh1-e1 exciton binding energy versus well width for $Zn_{0.69}Cd_{0.31}Se/ZnSe$ quantum well. Solid curves represent exciton binding energy as obtained with Luttinger parameters derived by Hölscher *et al.* (Ref. 17) and using Aldrich and Bajaj V_{AB} potential (upper curve) or Coulomb potential V_C (lower curve). Dashed curves represent exciton binding energy as obtained with Luttinger parameters derived by Sermage and Fishman (Ref. 18) and using V_{AB} potential (upper curve) or V_C potential (lower curve). Solid squares represent experimentally measured binding energies for 4 nm and 5 nm quantum wells. Bottom part: Calculated values of $2S$ binding energy versus well width with Luttinger parameters derived by Holscher *et al.* and using V_{AB} potential (upper curve) or Coulomb potential V_C (lower curve).

Figure 2 shows the peak energy positions of heavy- and light-hole excitonic states (solid circles) as a function of B for the sample with $L_w=5$ nm (a) and $L_w=4$ nm (b). From the extrapolated values of the $2S$ positions to $B=0$ we can determine the energy difference between the binding energies of $1S$ and $2S$ states. We can thus determine the binding energy of the $1S$ state of the hh exciton E_b^{1S} adding the calculated values of E_b^{2S} (shown in the bottom part of Fig. 3) to this difference. Alternatively, we can deduce E_b^{1S} through a fitting procedure to the zero-magnetic field absorption spectra around the continuum edge. This procedure includes the $2S$ excitonic absorption whose peak energy and intensity have been determined by comparison with $B>0$ spectra. These two procedures yield the same values for E_b^{1S} ($E_b^{1S}=37.5\pm2.5$ meV and $E_b^{1S}=35.7\pm1.5$ meV for $L_w=4$ nm and $L_w=5$ nm, respectively).

We now turn to the theoretical analysis, which is based on a variational calculation of $1S$ heavy-hole exciton binding energy versus QW width. A correct description of polaronic effects requires an effective exciton Hamiltonian in which not only electron and heavy-hole band masses are replaced by the corresponding electron and hole polaron effective masses, but also the effective potential differs from the Cou-

lomb potential screened by the static dielectric constant ϵ_0.[3]

The excitonic Hamiltonian (apart from the electron and hole self-energy terms) can therefore be expressed as a sum of three terms:

$$H = H_1(z) + H_2(z) + H_{ex}(x,y,z), \tag{1}$$

where H_1 and H_2 describe the motion of electron polaron and hole polaron along the growth axis z and are given by a sum of the along z kinetic term and the confining potential. H_{ex} describes the internal motion of the exciton and includes the effective electron-hole interaction potential. The along z and in-plane heavy-hole masses are expressed in terms of the Luttinger parameter γ_1 and γ_2. For the effective interaction potential, we use the following two different forms. First, we consider the Coulomb potential screened by the static dielectric constant

$$V_C = -\frac{e^2}{\epsilon_0 r} \tag{2}$$

and additionally, we consider the potential V_{AB} derived by Aldrich and Bajaj[3] that takes into account polaronic effects[13]

$$V_{AB} = -\frac{e^2}{\epsilon_0 r} - \frac{e^2}{2\epsilon' r}[\exp(-\beta_1 r) + \exp(-\beta_2 r)] + \sum_{i=1}^{2} \frac{e^2 \beta_i}{2\epsilon'} \frac{\exp(-\beta_i r)}{1 + \alpha_i/12 + \alpha_i/(4+\alpha_i/3)}, \tag{3}$$

where $\beta_i = (2m_i\omega/\hbar)^{1/2}$, $\alpha_i = e^2\beta_i/(2\epsilon'\hbar\omega)$, $1/\epsilon' = 1/\epsilon_\infty - 1/\epsilon_0$, and $m_i^* = m_i(1+\alpha_i/12)/(1-\alpha_i/12)$; ω is the longitudinal optical (LO) phonon frequency, ϵ_∞ is the high-frequency dielectric constant, and m_i^* is electron (heavy-hole) polaron mass.

The variational solution is sought by minimizing the exciton binding energy with the following trial wave function:

$$\Psi(z_1,z_2,\rho,\phi) = F_1(z_1)F_2(z_2) \times \exp(-\lambda r - [\nu\rho^2 - \eta(z_1-z_2)^2]^{1/2}), \tag{4}$$

where $F_1(z_1)$ and $F_2(z_2)$ are ground-state eigenfunctions of the electron polaron and heavy-hole polaron Hamiltonians H_1 and H_2, respectively, $\rho^2 = [(x_1-x_2)^2 + (y_1-y_2)^2]$, and λ, ν and η are the variational parameters.

We would like to remark that the above model considers the electron(hole) interaction with bulk LO phonons. However, it has been pointed out by Mori and Ando,[14] that the effect of electron (hole) interactions with the distinct phonon modes of a QW on the exciton binding energies is expected to be almost the same as that of electrons (holes) interacting with bulk LO phonons as long as the binding energies are different from the phonon energies (off-resonance condition).

In our calculation, we have used the following values of various physical parameters for the $Zn_xCd_{1-x}Se/ZnSe$ QW's. Conduction-band offset $\Delta E_e = 0.230$ eV, heavy-hole valence-band offset $\Delta E_h = 0.115$ eV. These values have been recently measured by transport techniques.[15] Electron polaron mass for the barrier material $m_1^b = 0.155m_0$, electron polaron mass for the well material $m_1^w = 0.14m_0$, static dielectric constant $\epsilon_0 = 8.7$, high-frequency dielectric constant $\epsilon_\infty = 5.73$, LO phonon energy $E_{LO} = 31.7$ meV as determined by resonant Raman scattering,[16] Luttinger parameters $\gamma_1 = 2.45$ and $\gamma_2 = 0.61$. The values of the Luttinger mass parameters that we have used in our calculations are those determined by Hölscher *et al.*[17] in their two-photon magneto-absorption measurements of the $2P$ exciton system in ZnSe. The calculated $1S$ hh1-e1 exciton binding energy is shown in Fig. 3 (solid lines) as a function of the well width together with the experimental values (solid points). The upper (lower) solid line is obtained using $V_{AB}(V_C)$ interaction potential. We find that the values of the binding energies obtained using Coulomb potential are considerably lower than those obtained using V_{AB} potential, especially for narrow wells where the short- range terms in the expression of V_{AB} potential become more important. As clearly seen in Fig. 3 experimental values of the exciton binding energies agree very well with those calculated using V_{AB} potential. We remark, however, that higher values for the mass parameters for ZnSe ($m_1 = 0.16m_0, \gamma_1 = 4.30$ and $\gamma_2 = 1.14$) were derived by Sermage and Fishman[18] using Brillouin scattering. Calculated values of the $2S$ exciton diamagnetic shift based on the excitonic Hamiltonian with the V_{AB} potential and modified for the presence of perpendicular magnetic field (data not shown), reproduce well the experimental results shown in Fig. 2 with both sets of Luttinger parameters, although a slightly better agreement is found with the smaller values of γ_1 and γ_2. In order to check the impact of such a change on the E_b^{1S} results, we have also calculated the variation of the exciton binding energy as a function of well width with the Luttinger parameters proposed by Sermage and Fischman using V_{AB} (upper-dotted line in Fig. 3) and V_C (lower-dotted line in Fig. 3) potentials. We find that the values of the exciton binding energies thus obtained are always lower (by about 3-4 meV for the well widths studied here) than those determined by using the parameters proposed by Hölscher *et al.* The upper dotted curve, however, lies close to the experimental points thus indicating that conclusion on the relevance of polaronic coupling does not depend on the set of Luttinger parameters. The above results highlight the effect of the polaron-induced enhancement of the exciton binding energy and indicate that polaronic coupling cannot be neglected in determining the excitonic properties of these highly polar QW structures. They also demonstrate that V_{AB} potential provides an accurate description of these effects. Recently, Zheng and Matsuura[19] have calculated the effect of the exciton interacting with confined LO phonons, interface phonons and half-space phonons on its binding energy in QWs with finite potential barriers. The $1S$ heavy-hole excitonic binding energies for our heterostructure obtained by using their approach are considerably larger (by about 4–6 meV) than those calculated with the V_{AB} potential.

Finally, we want to remark that the $1S$ exciton binding energies here reported are substantially larger than values previously reported for the same samples through a detailed comparison between zero-magnetic field absorptions and variational calculations without the inclusion of polaronic effects.[5] The discrepancy stems from the use of effective potential without the inclusion of polaronic effects. Those calculations were based on the envelope function and effec-

tive mass approaches with Luttinger mass parameters derived by Sermage and Fishman.[18] They agree with the results here presented for the case of screened Coulomb potential V_C (lower dotted curve in Fig. 3).

In conclusion, we have shown that polaronic coupling profoundly influences the excitonic properties of polar QW's such as the $Zn_xCd_{1-x}Se/ZnSe$ systems here analyzed. We have used an excitonic Hamiltonian with an effective interaction potential first derived in Ref. 3 that takes into account polaronic effects. In order to test this model, the 1*S* exciton binding energies were derived through magneto-absorption measurements in quantum well samples with widths of 5 and 4 nm and Cadmium concentration of 0.31. We found that the polaronic effective potential offers a good description of the 1*S* exciton binding energies. Comparison with a nonpolaronic model based on Coulomb potential screened by static dielectric constant ϵ_0 allows to clearly evaluate the impact of such polaronic effects. Detailed analysis of diamagnetic shifts within a polaronic model will be presented elsewhere.

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