Polaronic Excitons in Zn$_x$Cd$_{1-x}$Se/ZnSe Quantum Wells

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We present a detailed investigation of excitonic absorption in Zn$_{0.69}$Cd$_{0.31}$Se/ZnSe quantum wells under the application of a perpendicular magnetic field. The large energy separation between heavy- and light-hole excitons allows us to clearly resolve and identify magneto-excitonic absorption resonant with the continuum edge of the $1S$ heavy-hole exciton. Experimental values of the exciton binding energy are compared with results of a theoretical model that includes the exciton-phonon interaction. The remarkable agreement found unambiguously indicates the predominant polaronic character of excitons in ZnSe-based heterostructures.

In recent years wide-gap II-VI semiconductor based 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 (QWs) in which excitonic recombination is dominant even at room temperature [2]. These systems also present other unique properties such as a strong exciton-phonon interaction which makes them ideal candidates for the investigation of these kind of interactions (from here on referred to polaronic effects) on the optical properties.

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., QWs. In fact in the numerous experimental analyses on excitonic effects in II-VI QWs [6–8], the role of polaron in determining the exciton binding energy was not adequately addressed, and was actually often overlooked. This was probably due to the 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 communication we address this issue by analyzing the magneto-absorption properties of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{ZnSe}$ QWs. Our results clearly 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 Aldhrich and Bajaj [11] within an envelope-function formalism it is possible to reproduce quantitatively our experimental results with no adjustable material parameters.

Samples studied were grown by solid source molecular-beam epitaxy on $\text{GaAs}(001)$ substrates. They consist of a 0.5-µm $\text{GaAs}$ buffer layer grown at 580 ºC followed by 1.5-µm-thick $\text{ZnSe}$ layer grown at 290º C. Ten $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{ZnSe}$ QW’s were then grown at 250º C with a 30-s interruption at each interface. A 500-nm-thick cap layer concluded the growth. $\text{ZnSe}$ barrier width is 30 nm, 2-, 3-, 4- and 5-nm-thick QWs were examined. In order to detect transmission signals, circular regions of about $6 \times 10^{-4} \text{cm}^{-2}$ were selectively removed using standard photolithographic and wet-etching techniques. Further details about these structures can be found in Ref. [12]. The separation between the energy positions of 1S heavy- and light-hole excitons caused by the compressive strain in the QWs, allowed us 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 $T=1.6K$ 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 ($\approx 1$ meV). Samples were mounted on a variable-temperature insert and magnetic fields $B$ between 0 and 10T were applied parallel to the growth direction. Magneto-absorption was studied using a 100W xenon lamp as the source. Light was focused and collected along the growth direction by optical fibers. Transmitted intensity was normalized to the incident
light in order to detect absorption changes.

Figure 1 shows typical spectra at T=1.6K for the sample with QW thickness $L_w = 5$ nm without (dashed line) and with an applied magnetic field (10 T, solid line). 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. The absorption of what is supposed to be the heavy-hole continuum edge is observed at around 2560 meV. Thanks to the high confinement potential, an additional higher-energy peak due to the 1S (hh2-e2) heavy-hole exciton \cite{13} is also observed.

Upon application of the magnetic field, the 1S heavy- and light-hole exciton peaks display a small blue-shift and no appreciable oscillator strength enhancement. This behavior is 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 non-monotonic behavior which may be linked to valence-band mixing effects \cite{7}. The heavy-hole continuum edge, on the contrary, is dramatically altered, and a sharp peak on its low-energy side gradually emerges with increasing magnetic fields (see the right panel of Fig. 1 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 $6T \leq B \leq 10$ 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 is in qualitatively agreement with theory developed in Ref. \cite{14}.

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 expected values of 1S and 2S position to B=0 we can determine the energy difference
between the binding energies of 1S and 2S states, adding the calculated values of $E_2^{2S}$ we can
determine the binding energy of the 1S state of the $hh$ exciton.

Our theoretical analysis based on variational calculation of 1S exciton binding energy versus quantum well width demonstrates the importance of polaronic effects in $Zn_xCd_{1-x}Se/ZnSe$ QW’s. A complete account of the polaronic effects leads to an effective Hamiltonian for the exciton in which not only electron and hole band masses are replaced by the corresponding electron and hole polaron effective masses but also the effective potential differs from the Coulomb potential screened by the static dielectric constant $\epsilon_0$ [4].

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

$$H = H_1 + H_2 + H_{ex}$$

where $H_1$ and $H_2$ describe the motion of electron polaron and hole polaron along the growth axis ($z$):

$$H_i = -\hbar^2 \frac{\partial^2}{2m^*_i \partial z^2} + V_i(z_i)$$

where $V_1(z_1)$ and $V_2(z_2)$ are the confining potentials for the electron polaron and the hole polaron respectively, and $m_1^*$ and $m_2^*$ are the electron and hole polaron masses along the $z$ axis.

The term $H_{ex}$ describes the internal motion of the exciton in the $x$-$y$ plane:

$$H_{ex} = -\frac{\hbar^2}{2\mu^*} \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) + V_{int}(r)$$

where $\mu^*$ is the reduced electron and hole polaron mass in the $x$-$y$ plane, $\rho$ and $\phi$ are polar coordinates in the $x$-$y$ plane and $r^2 = (z_1 - z_2)^2 + \rho^2$. Hole masses are expressed in terms of the Luttinger parameter in these formulas:

For the effective interaction potential $V_{int}$, we use the following two different forms. First we consider the Coulomb potential screened by the static dielectric constant i.e.

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

(4)
and second, we consider the potential \( V_{AB} \) derived by Aldrich and Bajaj [4] that takes into account the polaronic effects.

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

where:

\[
\beta_i = \left(\frac{2m_i \omega}{\hbar}\right)^{1/2}
\]

\[
\alpha_i = \frac{e^2 \beta_i}{2e' \hbar \omega}
\]

\[
\frac{1}{\epsilon'} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}
\]

\[
m_\alpha = m_0 \frac{1 - \alpha/12}{1 + \alpha/12}
\]

where \( \omega \) is the longitudinal optical phonon frequency, \( \epsilon_\infty \) is high frequency dielectric constant, and \( m_i \) is electron (hole) band mass.

In order to calculate the binding energy of 1S state of an exciton as a function of well width we follow a variational approach and use the following form of the trial wave function:

\[
\Psi(z_1, z_2, \rho, \phi) = F_1(z_1)F_2(z_2)\exp(-\lambda r - \nu \rho^2 - \eta(z_1 - z_2)^2)
\]

where \( F_1(z_1) \) and \( F_2(z_2) \) are ground state eigenfunctions of the electron polaron and hole polaron Hamiltonians \( H_1 \) and \( H_2 \) respectively.

The binding energy \( E_B \) of the 1S state of the exciton is then defined as:

\[
E_B = E_1 + E_2 - \min_{\lambda, \nu, \eta} \left( \frac{\langle \Psi|H|\Psi \rangle}{\langle \Psi|\Psi \rangle} \right)
\]

where \( E_1 \) and \( E_2 \) are ground state eigenvalues of the electron polaron and hole polaron Hamiltonians \( H_1 \) and \( H_2 \) respectively.
In our calculation we have used the following values of various physical parameters for the $Zn_xCd_{1-x}Se/ZnSe$ QW’s. Electron band offset $\Delta E_e = 0.230$ eV, hole band offset $\Delta E_h = 0.115$ eV, electron polaron mass for the barrier material $m_b^1 = 0.155m_0$, electron polaron mass for the well material $m_w^1 = 0.14m_0$, static dielectric constant $\epsilon_0 = 8.7$, high frequency dielectric constant $\epsilon_\infty = 5.73$, LO phonon energy $E_{LO} = 0.0317eV$, Luttinger parameters $\gamma_1 = 2.45$ and $\gamma_2 = 0.61$.

The results of the calculation of binding energy versus well width for both $V_C$ and $V_{AB}$ are shown in Figure 3. The use of simple screened Coulomb potential leads to essential underestimation of the exciton binding energy in $Zn_xCd_{1-x}Se/ZnSe$ QW’s. On the other hand, the values of binding energy obtained with $V_{AB}$ are in a good agreement with the experimentally measured binding energies for the samples with $L_w = 5$ nm and $L_w = 4$ nm.

In conclusion, we have measured ... Using variational approach, we have calculated the exciton binding energies for $Zn_xCd_{1-x}Se/ZnSe$ QW’s vs. quantum well width using both Coulomb potential screened by static dielectric constant $\epsilon_0$ and the potential $V_{AB}$ derived by Aldrich and Bajaj, that takes account of polaronic effects. The comparison of the calculated values of the exciton binding energy to the experimentally obtained binding energies for 4 nm and 5 nm quantum wells demonstrates that the potential $V_{AB}$ should be used in the calculations of binding energy in order to achieve a reasonable agreement with the experimental data and that the polaronic effects essentially influence physical properties of excitons in $ZnSe$-based heterostructures. Detailed investigation of the diamagnetic shift will be presented elsewhere.

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

FIG. 2. (a) and (b) Energy of exciton absorption peaks vs. magnetic field for both the two sample (circles). Oizontal arrows indicate continuum energy position calculated by the polaron-based model. Least-square fit 1s and 2s hh1-e1 are shown as dashed curves.

FIG. 3. Calculated values of exciton binding energy vs. well width for the Zn_{0.69}Cd_{0.31}Se/ZnSe quantum well. Solid line represent exciton binding energy as obtained using Coulomb potential $V_C$. Dashed line represent exciton binding energy as obtained using potential $V_{AB}$. Solid squares represent experimentally measured binding energies for 4 nm and 5 nm quantum wells.
Figure 2: Energy levels as a function of magnetic field. (a) 1S hh1-e1 and 2S levels. (b) 1S hh1-e1 and 3S levels. The data points are indicated with error bars.
