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# Hydrostatic-pressure studies of confined transitions in cubic $Zn_{1-x}Cd_xSe/ZnSe$ strained-layer quantum wells

R. J. Thomas, H. R. Chandrasekhar, and M. Chandrasekhar
*Department of Physics and Astronomy, University of Missouri–Columbia, Columbia, Missouri 65211*

N. Samarth, H. Luo, and J. Furdyna
*Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556*
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Photoluminescence spectra of cubic $Zn_{0.82}Cd_{0.18}Se$ quantum wells of widths 30, 60, and 200 Å are studied as a function of hydrostatic pressure (0–60 kbar) at 80 K. The pressure coefficients of heavy-hole excitons are found to decrease with increasing well width. The photoluminescence energies of the ZnSe barrier and cap layers are also observed to shift as a function of hydrostatic pressure, providing a measure of the pressure coefficient of the direct gap in this material.

## I. INTRODUCTION

Wide-gap II-VI quantum-well structures derived from ZnSe have elicited interest for several years because of potential optoelectronic applications in the sub–500-nm spectral region. A recent breakthrough in materials development[1] has led to identification of a wide-gap heterostructure—$Zn_{1-x}Cd_xSe/ZnSe$—with the requisite optical properties for practical applications: specifically, this quantum-well system has shown both excitonic absorption[2] and low-threshold optically pumped lasing[3] at 300 K. Further, a $Zn_{1-x}Cd_xSe/ZnSe$ quantum well has been used as the active region of a blue-green diode laser.[4] The *fundamental* properties of this new heterostructure, however, remain relatively unexplored and it is important to carry out a variety of optical measurements in order to fully characterize this material.

We present a study of the effect of hydrostatic pressure (0–60 kbar) on the energy levels of cubic $Zn_{0.82}Cd_{0.18}$-Se/ZnSe quantum-well heterostructures at a temperature of 80 K. Three isolated quantum wells of cubic $Zn_{0.82}Cd_{0.18}Se$ of different widths separated by ZnSe barriers were grown on the same substrate. Such a sample has allowed us to determine the variations in pressure coefficients as a function of well width ($L_z$), along with those of the ZnSe barrier layers. The pressure coefficients of the $E_{1h}$ direct gap transitions are found to decrease with increasing well width, and are also smaller than that of the ZnSe barrier. We also observe a sizable decrease in photoluminescence (PL) intensity after roughly 50 kbar, which does not recover in the decreasing cycle of pressure (downstroke).

## II. EXPERIMENT

The heterostructures, grown by molecular beam epitaxy, consist of three single $Zn_{0.82}Cd_{0.18}Se$ wells of widths 200, 60, and 30 Å, separated by 500-Å ZnSe barriers. Because of the large barrier width, each well may be analyzed as an isolated quantum well. The quantum wells were grown on a 1-$\mu$m buffer layer of ZnSe on the (100) surface of a GaAs substrate. The ZnSe buffer layer is assumed to have properties of bulk ZnSe since it is thicker than the critical thickness ($\approx 0.15$ $\mu$m) for a pseudomorphic layer.[5,6] The widest well is closest to the buffer layer, allowing the upper layers to be transparent to the emission wavelengths of the lower wells. The final 30-Å well was capped with a 1000-Å layer of ZnSe. The alloy composition ($x = 0.18 \pm 0.02$) and the well widths ($\pm 5\%$) were determined from earlier calibrations of thick epilayers using lattice parameter measurements and step profilometry.

In order to perform studies under pressure, the GaAs substrate was thinned to about 30 $\mu$m and the sample ($150 \times 150 \mu m^2$) was placed in a Merrill Bassett gasketed diamond-anvil cell.[7] Argon was used as the pressure transmitting fluid. Fluorescence from the ruby $R_2$ line was used to calibrate the pressure.[8] The cell was attached to the cold finger of a cryostat and data were obtained at 80 K. PL was excited with approximately 5 mW of 3638-Å radiation from an argon-ion laser. The pressure was hydrostatic to at least $\pm 0.5$ kbar at the highest pressures, as observed by the linewidths of the ruby fluorescence peaks.

## III. RESULTS AND DISCUSSION

It is well known that in multilayer quantum-well structures, potential wells are formed, leading to quantized subbands whose energies are determined by the width and depth of the quantum well. Strongly allowed transitions occur between the quantized levels in the conduction band and the heavy-hole ($E_{nh}$) and light-hole ($E_{nl}$) subbands of the same quantum number $n$. The $E_{1h}$-$E_{1l}$ separation in these samples is rather large[2] (approximately 90 meV for a $Zn_{0.76}Cd_{0.24}Se/ZnSe$ multiple quantum well at 100 K). Therefore the thermal population effects make the $E_{1l}$ transition too weak to observe in PL.

 

The PL spectrum for the sample at 1 bar is shown in Fig. 1. The peaks $A$, $B$, and $C$ are the $E_{1h}$ transitions from the 200-, 60-, and 30-Å quantum wells, respectively. Also shown in the PL spectrum are peak $E$, the direct exciton emission from the ZnSe buffer, barriers and cap, and peak $D$, a deep level that may be due to donor-acceptor pair recombination in ZnSe. At 1 bar, we measure the relative intensities to be approximately 3:6:10 for A:B:C. The linewidths (full width at half maximum) of the peaks $A$, $B$, and $C$ are measured to be 6.1, 8.1, and 12.4 meV, respectively, confirming the high quality of the sample. The increase in linewidth with decreasing $L_z$ can be attributed to interface roughness. The relative intensities can be qualitatively attributed to absorption of the exciting radiation by the narrower wells closer to the surface and the intervening barriers and also to increased quantum efficiency due to confinement. The relative intensities of the peaks are not corrected for the spectral response of the monochromator and detector. The inset in Fig. 1 shows a schematic of the sample as described in Sec. II.

Figure 2 shows the effect of pressure on the $E_{1h}$ transitions in the three wells at 80 K, the pressure dependence of the ZnSe barrier, and the deep level of ZnSe. The lines through the data for peaks $A$–$D$ are due to least-squares fits to the function

$$E(P)=E(0)+\alpha P\,, \tag{1}$$

while the peak $E$ which corresponds to the ZnSe was fit to the function

$$E(P)=E(0)+\alpha P+\beta P^2 \tag{2}$$

due to its appreciable nonlinear behavior. The energies are in eV and the pressure $P$ is in kbar. The linear and nonlinear pressure coefficients ($\alpha$ and $\beta$) obtained are shown in Table I along with the zero pressure transition energies. The $\alpha$ and $\beta$ values for ZnSe are in good agreement with those for bulk ZnSe given in Ref. 9.

A systematic decrease in $\alpha$ with increasing well width is observed. This difference is demonstrated graphically in Figs. 3 and 4. Figure 3 shows spectra at three pressures, where the abscissa is for 1-bar data and the two spectra at the higher pressures have been shifted in energy such that peak $C$ from the 30-Å well at 12.1 and 31.9 kbar is aligned with that in the 1-bar spectrum. The vertical lines are a guide to the eye and demonstrate that the energy shift with pressure is *smaller* for well $B$ and the smallest for well $A$. Figure 4 shows this trend via the energy separations between the peaks $C$ and $A$, $C$ and $B$, and $B$ and $A$ as a function of pressure. The lines shown are results of linear least-square fits to the data. The figures clearly indicate that the energy separation increases with pressure, implying a decrease in $\alpha$ with increasing well width.

The above effect, though small, is a real effect outside the experimental uncertainty. Since all three quantum

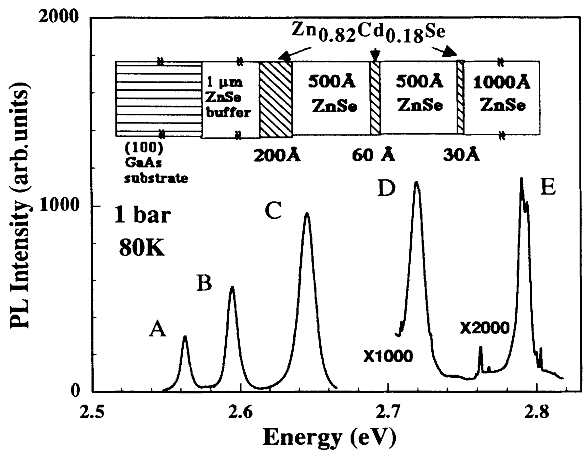


FIG. 1. PL spectrum of $Zn_{0.82}Cd_{0.18}Se$/ZnSe heterostructure at 80 K. A schematic of the sample is shown at top. The peaks $A$, $B$, and $C$ are the $E_{1h}$ transitions from the 200-, 60-, and 30-Å quantum wells. The peaks $D$ and $E$ are due to a deep level and the band-edge exciton in ZnSe.

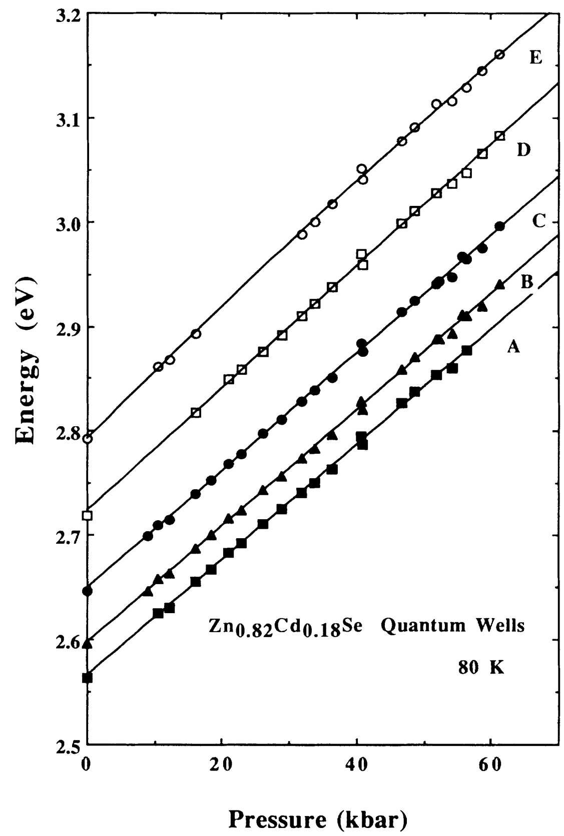


FIG. 2. Energies of the peaks $A$–$E$ of Fig. 1 as a function of pressure. The lines shown are results of least-squares fits to the data.

TABLE I. Pressure coefficients.

| | $E(P=0)$ (eV) | $\alpha$ (meV/kbar) | $\beta$ (meV/kbar$^2$) |
|---|---|---|---|
| $A$ (200 Å) | $2.5655\pm0.0013$ | $5.52\pm0.04$ | ... |
| $B$ (60 Å) | $2.5970\pm0.0012$ | $5.56\pm0.03$ | ... |
| $C$ (30 Å) | $2.6489\pm0.0013$ | $5.62\pm0.03$ | ... |
| $D$ | $2.7236\pm0.0019$ | $5.84\pm0.05$ | ... |
| $E$ (ZnSe) | $2.7971\pm0.0024$ | $6.47\pm0.19$ | $-0.0077\pm0.0030$ |

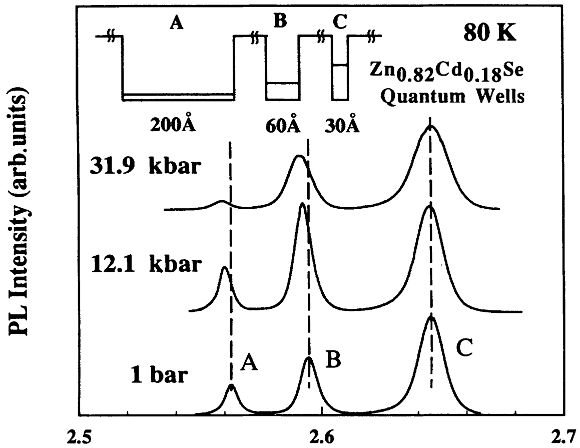


FIG. 3. PL spectra for the three quantum wells at various pressures and 80 K. The abscissa is for 1-bar data and the upper two spectra have been shifted to align peak $C$ in all three spectra. The vertical lines demonstrate that the energy shift is smaller for $B$ and smallest for $A$. The inset is a schematic of the conduction band in the three wells illustrating the differences in confinement energies.

wells are grown on the same substrate, one can measure the transition energies for all of them and the differences at the *same* pressure. The energy positions are accurate to $\pm 0.5$ meV which translates to 0.02%. Due to the Lorenzian line shape and the high signal-to-noise ratio in the data, the peak positions obtained from the fits retain the accuracy at high pressures despite some broadening. It is assumed that the observed increase in linewidth with pressure does not significantly alter the relationship of peak energy to transition energy. The plot of the energy *differences* of pairs of quantum wells versus pressure,

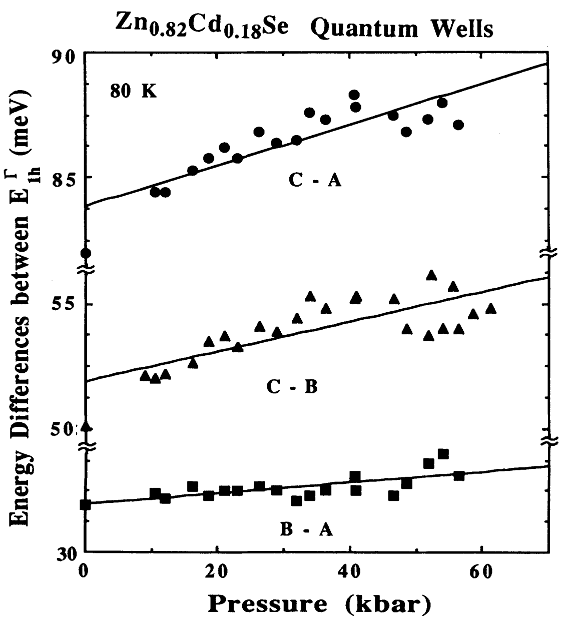


FIG. 4. Energy difference of the $E_{1h}$ transitions between pairs of quantum wells vs pressure at 80 K.

shown in Fig. 4, would have shown a zero slope if the $\alpha$ were the same for different well widths. It is clearly not the case as shown by the lines passing through the data which are due to the least-squares fits. Furthermore, the slope of ($C$-$A$) is larger than that of ($B$-$A$) indicating the effect to be larger for the narrowest well (30 Å). The slopes of the lines in Fig. 4 directly give the *differences* in $\alpha$. This analysis is superior to that of obtaining $\alpha$ for each well separately and taking the difference. The statistical errors due to the uncertainty in the measurement of pressure are not compounded in Fig. 4 because all three peaks see the same pressure due to the unique feature of containing the three wells in the same sample.

Similar effects have been observed in systems involving III-V materials. In contrast to the present study, $\alpha$ in the $GaAs/Al_{1-x}Ga_xAs$ system was found to decrease with decreasing well width.[10] On the other hand, the $In_{1-x}Ga_xAs/GaAs$ system[11] gives the same trend for $\alpha$ as in the present study.

There are several effects that influence the $L_z$ dependence of $\alpha$. The one-band Wannier orbital calculations of Ting and Chang[12] and Lefebvre, Gil, and Mathieu[13] for the $GaAs/Al_xGa_{1-x}As$ system has shown that the dominant effects are the increase in the electron effective mass ($m_e^*$) with pressure[14] for wide quantum wells, and the mixing of quantum well and barrier wave functions for narrow quantum wells. Therefore, one expects the $\alpha$'s to approach the barrier (well) $\alpha$'s for narrow (wide) quantum wells, which is indeed the case in $GaAs/Al_xGa_{1-x}As$. This trend is also seen in our present sample.

We have performed a calculation, similar to that in Refs. 12 and 13, in which the variation of the $m^*$ and $L_z$ are incorporated. We find that $\alpha$'s for peaks $C$ (30 Å) and $B$ (60 Å) *decrease* by 0.025 and 0.015 meV/kbar, respectively, whereas peak $A$ (200 Å) is not affected. From an eight band $\mathbf{k}\cdot\mathbf{p}$ calculation using the bulk-band parameters, we find that 23% of the electron wave function resides in the barrier for the narrowest well ($C$). The corresponding numbers for wells $B$ and $A$ are 6% and 2%, respectively. The wave functions of the holes are localized in the wells. The $\alpha$ would then be a weighted average of those of the well ($Zn_{1-x}Cd_xSe$) and the barrier (ZnSe), the weight factors determined from the above model calculation. Subtracting the decrease in $\alpha$ due to the variation of the $m^*$ and $L_z$, we obtain values of 5.52, 5.53, and 5.62 meV/kbar for wells $A$, $B$, and $C$, in excellent agreement with the measurement. We also deduce the $\alpha$ of bulk $Zn_{0.82}Cd_{0.18}Se$ in the cubic phase as 5.51 meV/kbar, close to that of the widest well $A$ which has the least admixture with the barrier. No other measurement of $\alpha$ for bulk $Zn_{0.82}Cd_{0.18}Se$ is available at present.

We note that in the $GaAs/Al_xGa_{1-x}As$ system, the increase of $m_e^*$ and wave-function mixing both decreased $\alpha$ for decreasing $L_z$, since $Al_xGa_{1-x}As$ has a lower $\alpha$ than GaAs. In the present sample, on the other hand, ZnSe has a larger $\alpha$ than $Zn_{0.82}Cd_{0.18}Se$, and the effect of wave-function mixing is to increase $\alpha$, as opposed to the decrease due to changes in $m_e^*$ and $L_z$, causing a net increase in $\alpha$ for decreasing well width.

There are other effects that are less dominant than those mentioned above, but which should be included in a full calculation. Differences in $\alpha$'s of bulk $Zn_{0.82}Cd_{0.18}Se$ and ZnSe result in a change in the well depth. Since $\alpha$ is larger for the ZnSe, one would expect the wells to become deeper with applied pressure, resulting in a decrease in $\alpha$ due to decreasing confinement energy. Another mechanism which must be considered is the exciton binding energy ($E_B$) as a function of pressure. Magneto-optic experiments have shown that $E_B$ increases with decreasing $L_z$.[15] The increase in $m_e^*$ reduces $E_B$ in the quantum wells. No detailed calculation exists for this material at the present time.

The intensity of the PL signal from the sample was observed to decrease to roughly one-tenth of its original value in the range of 45 to 60 kbar. The linewidths of the PL peaks also nearly double in this range. When the pressure is again reduced, these parameters fail to fully recover their values. This phenomenon is reminiscent of a phase change in the material.[7,16] However, our recent measurements on bulk $Zn_{0.82}Cd_{0.18}Se$ show no structural phase transition at least up to 76 kbar. The transition in ZnSe occurs above 100 kbar. We note that phase transitions in quantum-well structures occur at pressures different from those of the component materials in their bulk state, due to superpressing, as has been observed in GaAs/AlAs (Ref. 17) and CdTe/ZnTe (Ref. 18). Since the effect we observe is not at a pressure intermediate to the phase transition pressures of the well and barrier materials, the observed effect is unlikely to be caused by a structural phase transition. It may, however, be due to the formation of interfacial dislocations in the wide well whose thickness is close to the pseudomorphic limit at 1 bar.

Another explanation for the decrease in PL intensity might be a surface deterioration similar to that observed by Mei and Lemos[16] in their study of bulk (wurtzite) CdSe. However, our incident power is the same as that prescribed as nominal by their experiment, and did not produce any deterioration in 1-bar samples which were exposed to as much as 10 mW for several hours during initial PL measurements.

We have also ruled out the possibility of an indirect level crossing in the $Zn_{0.82}Cd_{0.18}Se$ wells as the cause for our loss of intensity. The intensities in the down stroke should recover when a level crossing occurs.[10] The exception to this would be if a pressure-induced trapping state was present in ZnSe or $Zn_{0.82}Cd_{0.18}Se$. This effect has been observed in a PL experiment in $Al_xGa_{1-x}As$ and the $GaAs/Al_xGa_{1-x}As$ system under hydrostatic pressure.[19] In the above experiment there is a hysteresis in pressure versus intensity, but even in that case, the intensity does in fact recover at low pressure. Also, we know of no states of this nature in experiments on bulk ZnSe or bulk $Cd_{1-x}Zn_xSe$.

## IV. CONCLUSIONS

A study of the pressure dependence of $Zn_{0.82}Cd_{0.18}$-Se/ZnSe heterostructure has shown that the pressure coefficients ($\alpha$) exhibit a decrease with increasing well width ($L_z$). By using a sample containing wells of different $L_z$ grown on the same substrate, these differences in $\alpha$ are measured directly. Various possible mechanisms responsible for this effect are discussed. Further studies at higher pressures on similar samples are in progress.

## ACKNOWLEDGMENTS

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