Exciton-binding-energy maximum in $Ga_{1-x}In_xAs/GaAs$ quantum wells

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The theoretically predicted peaked nature of the exciton binding energy as a function of quantum-well width has been experimentally observed. The values are obtained directly from interband magneto-optical measurements and compared with calculations based on the envelope-function method. The high quality of the samples is demonstrated by the fact that transitions involving Landau quantum numbers up to eight are seen in all wells and are identifiable at magnetic fields below 1 T. This unusually low scattering rate has allowed the binding energies to be obtained at a high degree of accuracy.

I. INTRODUCTION

The enhancement of the exciton binding energy in quantum wells (QWs) over comparable bulk semiconductors allows strong nonlinear effects in interband absorption to persist up to room temperature. In the case of a purely two-dimensional crystal this enhancement is calculated to be exactly fourfold;[1] however, calculations that take into account the heterostructure nature of the system show that such an enhancement is not fully realized. As long ago as 1983, Greene and Bajaj[2,3] presented variational calculations which showed that the exciton binding energy E_{BE} of $GaAs/Ga_{1-x}Al_xAs$ quantum wells peaked at a finite width, their calculations predicting that for low alloy concentrations x this peak could occur at a well width of 10 or more monolayers. The peaked nature of the binding energy is also a feature of envelope-function-based calculations, such as those presented here, and calculations based on direct numerical integration of an appropriate Hamiltonian.[4] Although many experimental studies have shown an increase in the binding energy as the well width z is reduced below $\simeq 10$ nm, the maximum in $E_{BE}(z)$ has not been observed. Recently, Moore *et al.*[5] reported photoluminescence excitation measurements on thin $Ga_{1-x}In_xAs/GaAs$ single quantum wells ($z<5$ nm) which importantly showed a positive dE_{BE}/dz and so it became clear that a maximum did exist. Measurements on superlattices of similar composition have also been performed[6] but these show a much reduced value of E_{BE} compared with single wells. Another relevant publication is that of Hou *et al.*[7] in which the exciton binding energy of three isolated wells with a lower indium mole fraction of 13% was measured using a very similar magneto-optical technique to that presented here. They observe only the usual negative dE_{BE}/dz region mentioned above, but it should also be noted that they have used the photoluminescence *emission* energy to obtain E_{BE} whereas it is the *absorption* energy that must be used. As a consequence, these authors will have overestimated E_{BE} by an amount equal to the Stokes shift, which has a value of between 2.1 and 5.1 meV in the samples studied here. Taking this into account places their values of E_{BE} below those presented here, which is in line with what one would expect for wells with lower indium mole fraction. The origin of the Stokes shift is not fully understood but it is also a feature of $GaAs/Ga_{1-x}Al_xAs$ QWs, where it has a similar value.[9]

From the previous results it is clear that a peak in $E_{BE}(z)$ must exist and in this paper we present magneto-optical data from four quantum wells of widths 3 to 11 nm, all of the same composition, which determine the maximum in $E_{BE}(z)$ for the first time in any quantum-well system and thus vindicate the longstanding theoretical predictions. The binding energies obtained are then compared with envelope calculations based on the envelope-function method.

II. EXPERIMENT

Two samples were studied in these experiments, both of which were grown by molecular-beam epitaxy (MBE) on [100] oriented GaAs substrates. One sample contained four $Ga_{1-x}In_xAs/GaAs$ single QWs of 3, 4, 6, and 12 nm thickness, each separated by 50 nm of GaAs, and the second contained a single QW of width 11 nm, grown immediately subsequent to the first and under nominally identical conditions. Because of the lattice mismatch, the $Ga_{1-x}In_xAs$ layers are under biaxial compression and are assumed to be tetragonally distorted. The total thickness of the $Ga_{1-x}In_xAs$ layers is such that the GaAs remains unstrained. It is noted that the multiwell has

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been the subject of previously reported high-pressure photoluminescence measurements.[9]

To perform the photoluminescence, photoluminescence excitation (PLE), and interband magneto-optical measurements, the samples were cooled to either 4.2 K or 2 K and excited with a Spectra Physics model 3900 Al_2O_3:Ti laser which has a measured spectral linewidth of approximately 0.05 meV (10 GHz). The Al_2O_3:Ti laser energy was continuously monitored by splitting off a small portion of the beam into a Burleigh rapid scanning Michelson-Morley interferometer. The luminescence was dispersed with a 0.85-m focal length SPEX spectrometer and detected with either a Peltier-cooled Hamamatsu R943-02 GaAs photomultiplier operating with photon counting electronics or with a North Coast liquid-nitrogen-cooled Ge pin detector operated with a lock-in amplifier.

Zero-magnetic-field photoluminescence measurements reveal a single intense, sharp feature from each well, as shown in Fig. 1. This is assigned to free excitonic emission associated with recombinations between the lowest confined electron and highest heavy hole ($m_j = \pm\frac{3}{2}$) states in the $Ga_{1-x}In_xAs$ wells and has a full width at half maximum of between 2.5 and 3.8 meV depending on the well. No other well emissions are seen. When a magnetic field B is applied, the diamagnetic shift is observed to be very small, as it is in $GaAs/Ga_{1-x}Al_xAs$ QWs, having a value of order 0.5 meV at 3 T, increasing superlinearly to approximately 2 meV at 6 T for all four wells. Consequently, when the well is illuminated with monochromatic radiation of energy greater than the absorption edge and the magnetic field is scanned, the oscillations in absorption are readily detected through the change in the ground-state luminescence intensity. This effect has been previously reported in lattice-matched $GaAs/Al_xGa_{1-x}As$ quantum-well structures.[10] These magnetoluminescence oscillations (MLOs) are in some ways the two-band analog of Shubnikov–de Haas or de Haas–van Alphen oscillations, as discussed elsewhere.[11] Figure 2 is typical of the MLOs that we observe, and by performing such scans for a range of incident excitation energies, the luminescence peak positions as a function of magnetic field are obtained. These results are summarized in Fig. 3. A comparison of our results with true absorption measurements on similar wells[12] confirms the fact that the peaks in luminescence intensity correspond to peaks in absorption, as might be expected, and we call these peak positions "transitions" for the remainder of the paper. Further, we assign all the observed peaks to $\Delta n = 0$ transition between the same electronic subband states.

It is noted that as the ground-state transition energy is only very weakly varying with B, the laser energy has been scanned for fixed B to obtain these points. Further, although there is a small Stokes shift of around 2 meV at $B = 0$, it is necessary to monitor the low-energy tail of the luminescence to obtain these $n = 0$ transitions, whereas for all the other transitions the luminescence *peak* can be monitored. Physically, scanning the laser energy at various fixed magnetic-field values, as performed extensively by Maan and co-workers[13] is fully equivalent to the measurements presented here. The reasons we have instead chosen to scan the field are as follows. Firstly, operating at a fixed energy allows the $1/B$ of the MLOs to be more readily studied, and one immediate advantage here is that Landau-quantum-number assignment can be made from each individual scan by plotting the peak positions

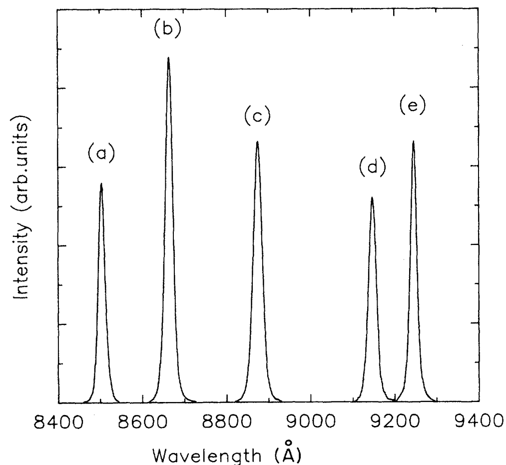

FIG. 1. Excitonic photoluminescence from the wells of width (a) 3 nm, (b) 4 nm, (c) 6 nm, (d) 11 nm, and (e) 12 nm, where the peak intensity occurs at 1.458, 1.431, 1.397, 1.356, and 1.341 eV, respectively, with full width at half maxima of 3.1, 3.4, 3.8, 3.2, and 2.5 meV. The luminescence was excited with laser energies above that of the GaAs band gap with power densities of less than 1 mW cm^{-2}. No other well emissions were observed. The data have been corrected for the spectral response of the detector.

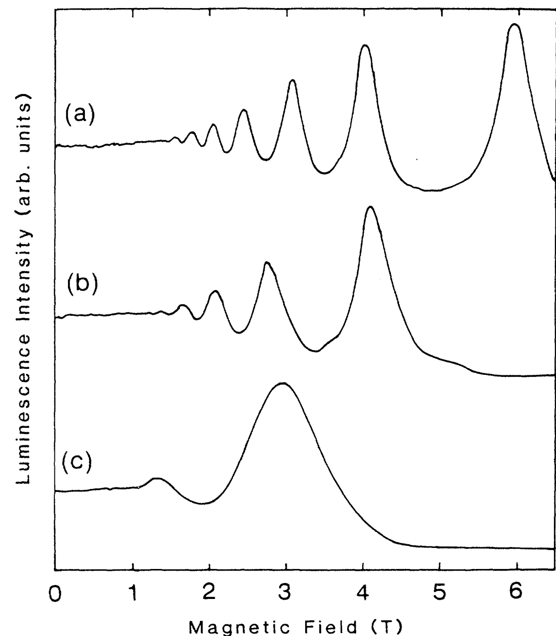

FIG. 2. Magnetoluminescence oscillations for the 3-nm well for three different incident laser energies at (a) 37 meV, (b) 28 meV, and (c) 14 meV from the excitonic absorption peak. The other wells show very similar behavior.

against $1/B$ as is the normal procedure in Shubnikov–de Haas measurements. Secondly, operating at a fixed wavelength allows the laser energy to be continuously monitored throughout each scan, giving an accuracy of better than 0.02 meV. To obtain a comparable accuracy while scanning the laser over the necessary energy range is more difficult, since the scanning mechanism produces a variation in wavelength that is slightly nonlinear as a function of time.

III. ANALYSIS

The exciton-binding-energy values plotted in Fig. 4 are obtained by taking the difference in energy between the excitonic absorption peak measured at $B=0$ and the intercept of the higher-Landau-quantum-number transitions ($n>4$) extrapolated back to $B=0$. More precisely, the intercept value obtained is the mean over those transitions which are seen to converge (that is, from $n=4$ up to the maximum n observed) and the error in this intercept is taken as the standard deviation of these various energies divided by the square root of the number of transition used (for example, 7 in the case of $n=4$ to $n=10$). This error is then combined with the uncertainty of the photoluminescence excitation measurement of the excitonic peak energy to obtain the total error shown in Fig. 4. It is noted that in the 12-nm well only transitions up to approximately $n=5$ are clearly observed and hence an accurate measurement of the high-n intercept was not possible by the above method. However, using only the $n=4$ and $n=5$ intercepts, the binding energy is estimated to be 6 ± 1 meV.

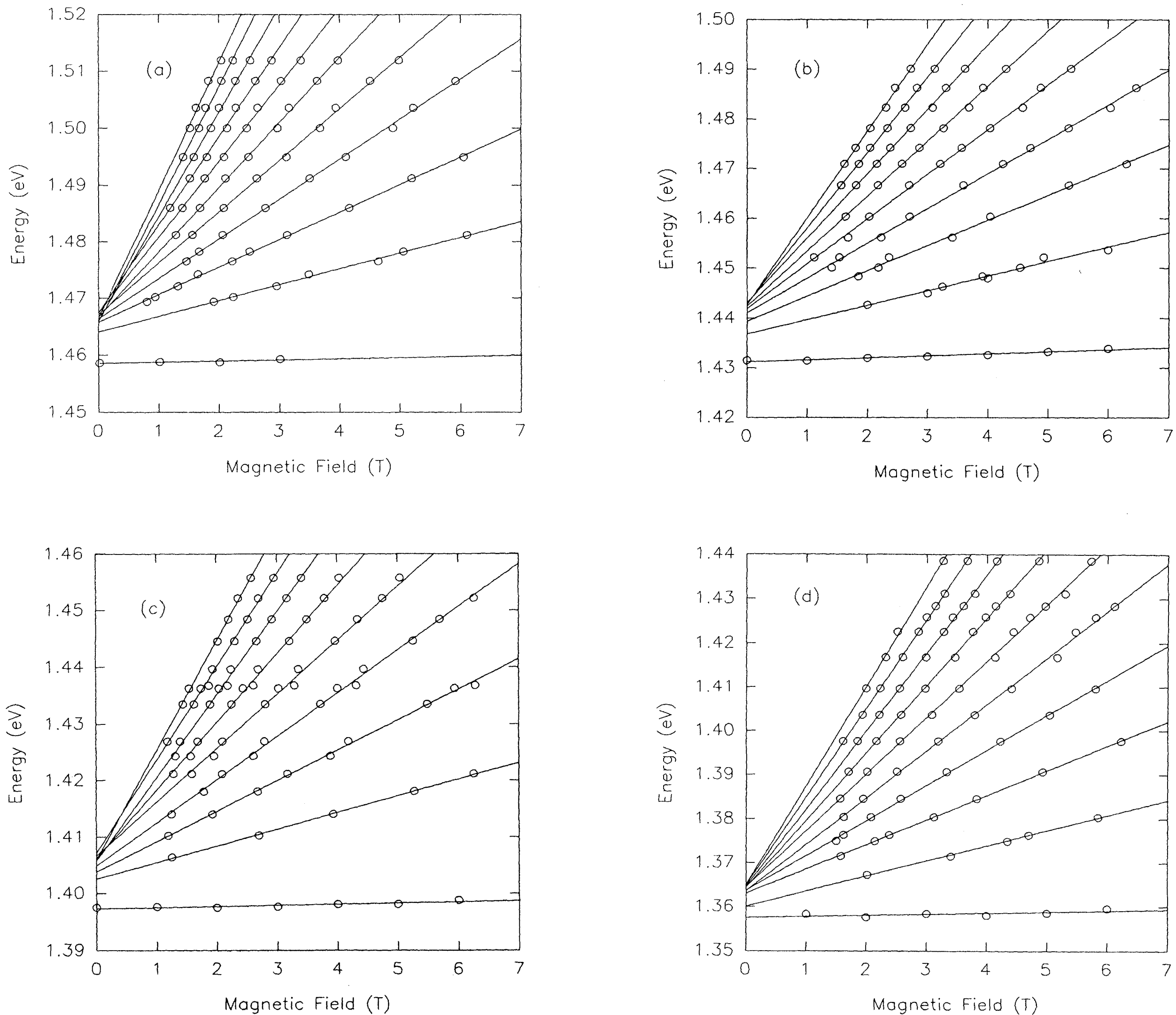

FIG. 3. Interband transition energies as a function of magnetic field for the wells of width (a) 3 nm, (b) 4 nm, (c) 6 nm and (d) 11 nm, where the circles represent measured values and the solid lines are linear least-squares fits to transitions involving the same Landau quantum numbers n. The reduction in intercept energy for $n<3$ and the close convergence of intercepts for higher n are noted.

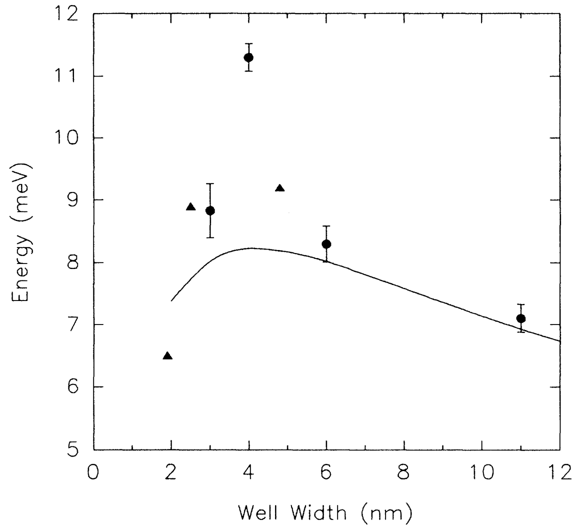

FIG. 4. Variation in exciton binding energy as a function of well width where circles are from this paper and the error determination procedure is detailed in the text. The triangles are from Ref. 5 where no errors are given.

The theoretical foundation of the method described above is well established and is based on treatments of the hydrogen atom in a magnetic field.[14–16] These show that the Coulombic contribution to the energy eigenvalue decreases rapidly as the Landau quantum number increases so that the higher-order Landau levels have an almost convergent zero-field intercept. This is shown very clearly, in a self-consistent manner, in all the wells studied, as can be seen from the solid lines in Fig. 3. These lines are simply linear least-squares fits to $\Delta n = 0$ transitions between states of like n and are seen to converge to a common intercept as n increases. It is noted that although convergence does occur, the reduction in Coulomb energy with increasing n is much less rapid than predicted theoretically, the relative spacing between the intercepts of the $n = 0$ 1, and 2 transitions being consistent with a $1/n^2$ or similar progression of the Coulombic contribution rather than the $1/(n+\frac{1}{2})^3$ relationship predicted.[16] The use of linear interpolation may seem at first sight to be simplistic in the extreme. However, apart from the self-consistent agreement manifested by the intercept convergence which is seen in all four wells, it is also noted that there is no systematic divergence from the linear fit either with the varying well widths or n over the wide range of energies studied. Additionally, when the interband reduced masses μ for the $n > 4$ transitions are calculated by only taking into account the Landau energies, all the values obtained agree to within $\pm 2\%$ for any given well. These interband reduced masses as well as other electron-mass measurements that we have performed on these wells are discussed elsewhere.[17]

We attribute the satisfactory use of such an approach to the simplification of the valence subband structure arising from the built-in axial strain of the $Ga_{1-x}In_xAs$ QWs. This strain splits the degeneracy of the valence-band maximum and for a layer under biaxial compression, as here, the highest valence states are derived from the $|\frac{3}{2}, \pm\frac{3}{2}\rangle$ bulk states, which are now only weakly coupled to the $|\frac{3}{2}, \pm\frac{1}{2}\rangle$ states. This reduced coupling has been shown experimentally and theoretically to lead to a simple, approximately linear relation between cyclotron resonance frequency and magnetic field B in a modulation p-doped $Ga_{0.82}In_{0.18}As/GaAs$ sample of well width 9 nm.[18] By contrast, it is essential to include valence-band mixing in the interpretation of intraband and interband magneto-absorption in both $GaAs/Ga_{1-x}Al_xAs$ QWs (Ref. 19) and bulk GaAs,[20] where strong hybridization effects between $m_j = \pm\frac{3}{2}$ and $m_j = \pm\frac{1}{2}$ states are important even at low B. We also note that our recent results on a similar multisingle QW sample with indium mole fraction $x \simeq 0.3$ show the same characteristics.

The effect of conduction-band nonparabolicity is weak in $GaAs/Ga_{1-x}Al_xAs$ quantum wells and can be expected to be, at most, of comparable strength in InGaAs. Using the experimentally deduced value[19] of -1.2 for the nonparabolicity parameter K_2 and assuming the pseudomomentum in the growth direction to be zero, one finds the change in conduction-band eigenenergy ΔE to be given by $\Delta E = -cE_e$, where E_e is the electron energy in the conduction band and c is a constant for any given n proportional to $(n+\frac{1}{2})$. For the transitions observed, this gives a maximum value of $\Delta E/E_e$ of about 4%. The nonparabolicity is also expected to raise the value of the $B = 0$ intercept as n increases. However, this is clearly not seen. In other words, using the $GaAs/Ga_{1-x}Al_xAs$ value for the K_2 parameter, we estimate the effect to be quite small and from the behavior of the observed transitions it appears to be even smaller. As a check, we have confirmed this by fitting high-quantum-number wide-well transitions to a Pidgeon and Brown[21] model calculation using an appropriate number for the strain splitting of the valence bands.[18]

Also plotted in Fig, 4 is the calculated exciton binding energy as a function of well width for strained $Ga_{0.82}In_{0.18}As$ wells between unstrained GaAs barriers. The calculations were made using the variational-perturbational approach of Ekenberg and Altarelli.[22] This includes coupling between the light-and heavy-hole excitons and also includes the effects of conduction-band nonparabolicity. The material parameters used are given in Table I. The valence-band γ parameters and electron mass m_e for $Ga_{0.82}In_{0.18}As$ were calculated by linear interpolation between GaAs and InAs values[23] but allowing for the variation with strain of the light-hole and electron masses via the $\mathbf{k}\cdot\mathbf{p}$ interaction. The condition-band nonparabolicity terms in the alloy are assumed to be of the same magnitude as in GaAs.[24] The band offsets are calculated assuming a 65:35 ratio of the electron to heavy-hole offset and the electron light-hole offset is taken as being type I for computational convenience.

Excellent agreement is obtained between theory and experiment for the 6- and 11-nm wells. The calculations find the peak binding energy to occur at 4 nm, in agreement with experiment, but underestimate significantly the sharpness of the experimental peak. This may be related to a breakdown of the perturbational method used and

TABLE I. Parameters used in the exciton-binding-energy calculations.

Parameter	Symbol	Units	$Ga_{0.82}In_{0.18}As$	GaAs
Electron masses	m_e	$m_e^{0^{-1}}$	0.061	0.0665
Conduction-band nonparabolicity terms	α'	eV^{-1}	0.60	
	α_0	$eV\,cm^4$	-1.969×10^{-29}	
	β_0	$eV\,cm^4$	-2.306×10^{-29}	
Valence-band parameters	γ_1		7.61	6.85
	γ_2		2.33	2.10
	γ_3		3.12	2.90
Dielectric constant	ϵ		13.08	
Band offsets	Electron	meV	105	
	Heavy hole	meV	53	
	Light hole	meV	5	

also may reflect that the effective-mass approximation becomes less reliable for calculating in-plane dispersion for such thin wells.

The exciton binding energy was also calculated in the diagonal approximation, which ignores the coupling between heavy-hole ($m_j=\pm\frac{3}{2}$) and light-hole ($m_j=\pm\frac{1}{2}$) excitons. Compared with the more comprehensive theory, the calculated values were 0.54 meV lower at a well width of 11 nm and by as much as 1.02 meV at 4 nm. These results emphasize that some valence-band mixing still occurs in the QWs despite the strain-induced separation of the light- and heavy-hole states.

IV. DISCUSSION

It is important to compare the magneto-optical method used here with the zero-field method of Ref. 5. For example, in Fig. 5 we show the PLE measured over the absorption edge region for the 4-nm well, and it is apparent that the energy at which the onset of free carrier absorption occurs cannot be determined precisely. The procedure of Ref. 5 is to take the energy of the second peak as the absorption edge, but it is clear from this PLE data that the position can only be determined to approximately ±1 meV. However, the arrow in Fig. 5 comes from our data for the $B=0$ intercept of the higher Landau-quantum-number transitions, showing that the magneto-optical value lies near this second peak and thus is consistent with Ref. 5 while giving a much more precise determination of the absorption edge. Furthermore, the qualitative shape of the free carrier absorption does not correspond to the ideal, zero-scattering-rate joint density of states (DOS) since an abrupt steplike rising edge followed by a plateau is not observed. Instead, a rounded absorption is seen for all four wells studied here and this is also true, although to a lesser extent, of the data given in Fig. 3 of Ref. 5. Since even the qualitative shape of the PLE does not correspond to the zero-scattering-rate joint DOS, the basis of the above method is not clear in such samples. In particular, the mechanism that causes the luminescence intensity to drop at energies above the free carrier absorption edge is not apparent.

We conclude that less-disordered samples which have a zero-field joint DOS which more closely approaches the ideal are required before the zero-field method can be satisfactorily applied. By comparison, the magneto-optical method requires the observation of transitions with sufficiently high Landau quantum numbers to allow separation of the Coulomb contribution to the eigenvalues. It also requires that the transitions occur down to sufficiently low fields to make the extrapolation to $B=0$ reliable. On the basis of our data the conditions necessary to obtain a satisfactory result by the magneto-optical method appear to be less stringent than those for the zero-field method.

Finally, we note that for the 12-nm well the free carrier absorption edge was not observed, in contrast to the other four wells. This is consistent with the failure to observe Landau transitions of higher order than $n=5$ for this well, as discussed in Sec. 3.

V. SUMMARY

The predicted peak in exciton binding energy as a function of well width has been observed experimentally for the first time. The values are obtained directly from high-resolution interband magneto-optical measurements

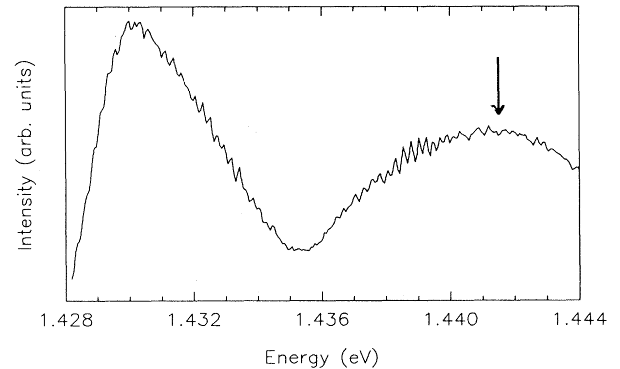

FIG. 5. Photoluminescence excitation of the 4-nm well in the region of the absorption edge. The value of the high-quantum-number transition energies extrapolated back to $B=0$ obtained from the magneto-optical method is indicated by the arrow. The "noise" is actually reproducible output-power fluctuations of the exciting laser.

using a simple least-squares analysis of the higher-Landau-quantum-number transition energies combined with a photoluminescence excitation measurement of the exciton emission energy. The validity of this simple analysis is confirmed in a self-consistent manner by the close convergence of the high-Landau-quantum-number intercepts, the nature of their reduction at low quantum numbers, and by the progression in dE/dB of the transitions. The validity of the analysis is also directly confirmed by a comparison of the observed transitions with 8×8 $\mathbf{k}\cdot\mathbf{p}$ model calculations.[21] When the exciton binding energies obtained experimentally are compared with a variational-perturbational[22] calculation, excellent agreement is found for the wider wells, but the theory underestimates the magnitude of the experimental peak, probably due to the omission of valence-band nonparabolicity parameters in the present calculations.

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