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High-pressure studies of GaAs-$Al_xGa_{1-x}As$ quantum wells at 300 and 80 K using photoreflectance spectroscopy

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A detailed photoreflectance study of a GaAs-$Al_{0.3}Ga_{0.7}As$ multiple quantum well of well width 260 Å is carried out at 300 and 80 K. The pressure dependence of a large number of quantized states is observed. The sublinearity of pressure dependence increases with increasing quantum number. A model calculation that includes the pressure dependence of electron effective mass accurately describes the data. Transitions associated with L and X band extrema are observed and their pressure coefficients deduced.

I. INTRODUCTION

Our previous photoreflectance (PR) and photoluminescence (PL) studies[1–5] of GaAs-$Ga_{1-x}Al_xAs$ superlattices under large hydrostatic pressures at cryogenic temperatures have yielded valuable information on the (a) effect of quantum confinement on the pressure coefficients, (b) the pressure dependence of X and L bands and associated impurities, and (c) an accurate determination of the band offsets. This work and related PL studies under hydrostatic pressures has stimulated considerable theoretical work.[6,7] An accurate theoretical description of the pressure dependence of the excitonic transitions, $CnHm$ and $CnLm$, in particular (for $n=m=1$), had yielded excellent agreement with the measured data.[6,7] The symbols refer to the transitions originating from the nth quantized state in the Γ conduction band (CB) to the mth state in heavy-hole (H) or light-hole (L) valence bands. In this paper we present the pressure and temperature dependence of quantum-well transitions for n up to 7 using the PR technique. We have also been able to obtain data on the transitions associated with the X- and L-band extrema. We have made calculations[8] in which the material parameters are included. We find that the change in the electron effective mass with pressure leads to a substantial sublinear pressure dependence of the quantum-well transitions. The effect is larger for higher-energy states. The calculation by Christensen[9] for the change in the electron effective mass with pressure gives a satisfactory fit to the observed data.

II. EXPERIMENT

The multiple-quantum-well (MQW) structure was grown on a semi-insulating GaAs substrate by the molecular-beam-epitaxy (MBE) technique. The sample consisted of 40 periods of 260-Å GaAs wells and 130-Å $Al_{0.3}Ga_{0.7}As$ barriers. The aluminum mole fraction was determined by Auger spectroscopy and confirmed by PL and PR from a reference sample grown under identical conditions. The well widths are estimated by the growth parameters and are consistent with the fit to the PL and PR spectra from finite-well calculations.[8] For pressure measurements the GaAs substrate was thinned to about 30 μm and the sample was placed in a gasketed diamond-anvil cell. Argon was used as the pressure-transmitting fluid. Fluorescence from the ruby R(1)-R(2) lines was used to calibrate the pressure. The cell was attached to the cold finger of a variable-temperature cryostat to obtain data in the (4–300)-K range. The pressure was hydrostatic to at least ±0.5 kbar as observed by the linewidths of the ruby peaks and the quantum-well transitions. PL was excited by the 5145-Å line from an argon-ion laser and analyzed by a Spex Industries double monochromator equipped with holographic gratings, cooled photodetector, and photon-counting electronics. The PR setup was similar to that described in the literature.[10] A quartz halogen lamp equipped with a stable power supply provided the radiation which was monochromatized by a Spex Industries (0.75-m) monochromator. Modulation was provided by chopped radiation from different laser lines of an argon-ion laser or a He-Ne laser. Both the beams were focused at the same spot on the sample. Due to the small size of the sample in the diamond-anvil cell (0.1 mm), a precise beam-steering and focusing optics with miropositioners was employed. The details of these systems are available in Refs. 4 and 5.

III. RESULTS AND DISCUSSION

The first study of the effect of hydrostatic pressure on the PR spectra of a GaAs-$Al_xGa_{1-x}As$ MQW of 400 Å well width at room temperature has been published elsewhere.[1] We recall a few results that are relevant to this work. A large number of parity-allowed and -forbidden transitions were observed. Their pressure dependence was linear at low pressures. At higher pressures a small sublinear pressure dependence was seen but could not be quantitatively analyzed due to the numerous overlapping peaks. In this study we have chosen a MQW with well width $L_z = 260$ Å. One can observe a large number of transitions in this sample. However, the principal peaks are sufficiently far apart for an accurate study.

Figure 1 shows part of the PR spectrum at atmospheric pressure and several temperatures. A large number of peaks are observed, which become sharper and readily resolved as the temperature is lowered. The numbered peaks are the strong ones which could be studied in detail under pressure. Noe that there are weaker peaks between 5 and 7a and 7 and 9a which become clear at temperatures below 150 K. There is an unresolved structure in the vicinity of peak 1. The identification of all the transitions in this rich and complex spectrum cannot be unambiguous. However, a careful analysis of (a) the relative intensities and temperature dependence[11], (b) comparison with experiment and model calculations which include mixing of valence subbands leading to strong parity forbidden transitions,[12] and (c) the structure (1*s*-2*s* splitting) in the excitonic transitions which has been reported in excitation[13] and PR spectra[14] has facilitated the identification of most peaks.

Table I shows the energy positions of prominent peaks at two different temperatures. The numbers in the column labeled "theory" are from a finite-potential-well calculation similar to that of Masselink *et al.*[12] The column labeled "Transition" identities the peaks in two different ways. The peaks indicated by "ex" in parentheses are the 1*s* excitonic transitions. Note that some peaks (e.g., 2–6) may be due to two separate transitions which are not resolved. Sanders *et al.*[12] have shown that the forbidden excitonic transitions $C1H2$, $C1H3$, and $C1L1$ may be unusually strong due to the hybridiza-

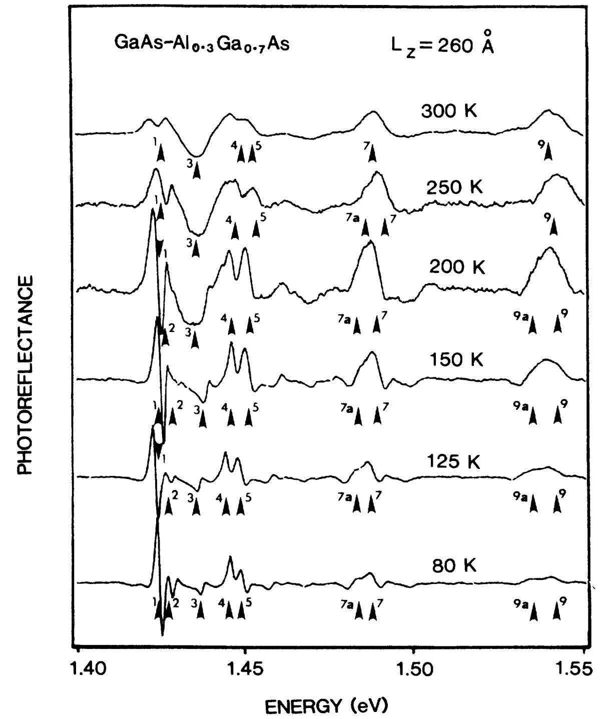

FIG. 1. Photoreflectance spectra of a GaAs-Al$_{0.3}$Ga$_{0.7}$As multiple-quantum-well structure at different temperatures. Note that the energy scale corresponds to the spectrum at 300 K. Other spectra have been shifted to align peak 1 in all the spectra. The numbers correspond to transitions described in Table I.

TABLE I. Experimental and calculated energy positions for transitions of a GaAs-Al$_{0.3}$Ga$_{0.7}$As MQW ($L_z = 260$ Å).

Peak no.	Transition	Energy (eV) 300 K Expt.	300 K Theor.	80 K Expt.	80 K Theor.
1	$C1H1$ (ex)	1.424		1.512	
2	$C1L1$ (ex)			1.515	
	$C1H2$ (ex)				
3	$C1H1$	1.435	1.432	1.524	1.516
	$C1H3$ (ex)				
4	$C2H2$ (ex)	1.446		1.534	
	$C2L1$ (ex)				
5	$C2H2$	1.455	1.455	1.538	1.539
	$C2H3$ (ex)				
6a	$C2L2$ (ex)			1.547	
6	$C2L2$	1.470	1.469	1.556	1.553
	$C1L3$ (ex)				
7a	$C3H3$ (ex)			1.570	
7	$C3H3$	1.490	1.491	1.578	1.575
9a	$C4H4$ (ex)			1.621	
9	$C4H4$	1.541	1.540	1.631	1.624
11	$C5H5$	1.598	1.599	1.680	1.683
13	$C6H6$	1.664	1.665		1.749
15	$C7H7$	1.731	1.733		1.817

tion of valence subbands. Peaks 2—4 correspond to these three transitions. Calculations extending to higher forbidden transitions are not available in the literature. Peaks 5 and 6 are close to $C2H3$ and $C1L3$ which are forbidden. We cannot find any reasonable combination of forbidden transitions for peaks 7–15 which agrees with the experiment.

The temperature dependence of peaks close to 4, 7, and 9 is very interesting, not to mention the dramatic change in the vicinity of peaks 1–3, where there are many possible transitions. Notice peak 7 at 300 K, which develops a shoulder, 7a, that grows in intensity with respect to 7 as the temperature is lowered. This structure is in agreement with the $C3H3$ transition. If we identify 7a as the 1*s* excitonic structure, we are left with 7, which does not correspond to any allowed or forbidden transition. The separation between 7a and 7 remains constant with temperature. The same happens to peaks 9a and 9, which have a well-resolved structure at 80 K. This behavior is very similar to that observed by Miller *et al.*, Meynadier *et al.*, Dawson *et al.*, and Koteles *et al.*[13] in photoluminescence excitation (PLE) and by Shen *et al.*[14] in photoreflectance and photoreflectance-excitation spectroscopy. They all observe structure in excitonic transitions and attribute it to the 1*s*-2*s* splitting of the excitonic structure. The higher transitions and the continuum structure are not resolved well enough to be identified. The 2*s* peak rises sharply and usually has a long tail on the high-energy side and is reminiscent of the continuum edge in the PLE spectra for samples in which the next-higher transition is well separated in energy. Due to the complicated line shapes in the PR spectra, it is not possible to distinguish the 2*s* peak from the continuum edge. Peaks 7 and 9 are thus identified as being associated with the excited-state features of $C3H3$ and $C4H4$ transitions. On the same basis, it seems that the excited-state structure of $C1H1$ and $C2H2$ should also be observable in the vicinity of peaks 3 and 5. It is not clear how much of peak 3 is due to this feature and the forbidden $C1H3$ exciton which coincides with it. Similar things happen to peak 5, which is close to the $C2H3$ exciton. This ambiguity, however, will not affect the conclusions on the pressure dependence of the MQE transitions.

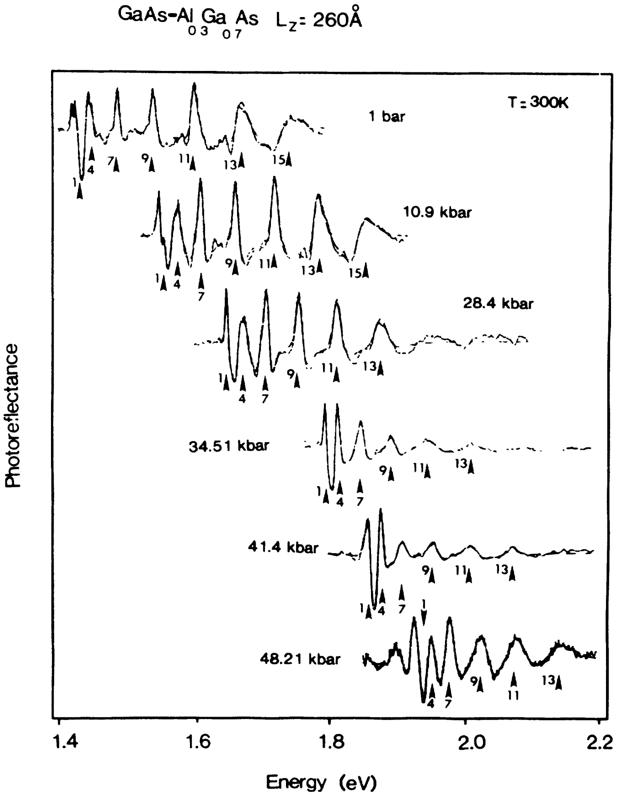

FIG. 2. PR spectra at 300 K and different pressures. The dotted curves are from a fit to the Aspnes third-derivative functional form. The numbers are identified in Table I.

A. Room-temperature studies

Figure 2 sows the pressure evolution of MQW transitions. The solid curves represent the experimental data. The dotted curves are from a fit to the Aspnes third-derivative functional form.[15] The peak positions, widths, amplitudes, and phases of the PR features are deduced from such fits. The identification of the transitions is consistent with Table I.

In a previous study[3] of the pressure dependence of $C1H1$ and $C1L1$ transitions in PL, it was shown that the pressure coefficient, α, was dependent on the confinement energy of the transitions. It was shown (Fig. 8 of Ref. 3) that α decreases by 5–6% from the bulk value as the well width was decreased to yield a confinement energy of 200 meV. This small effect could be accurately deduced by growing several quantum wells of different widths on the same substrate, so that the $C1H1$ transition energies

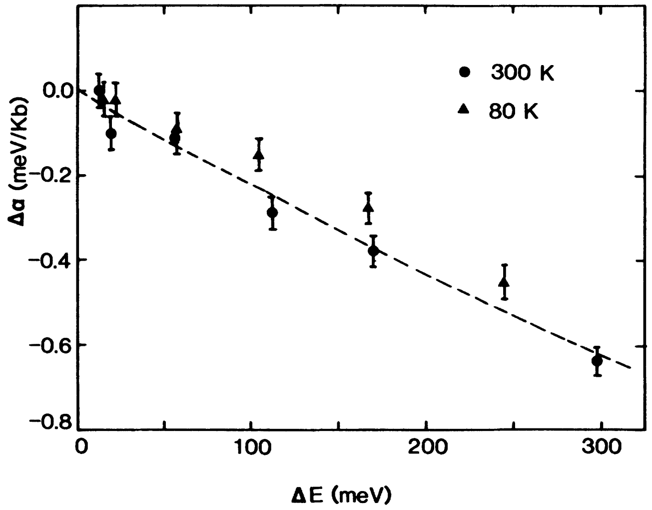

FIG. 3. Change in the pressure coefficient $\Delta\alpha$ vs the difference in energy ΔE expressed with respect to the corresponding values of the $C1H1$ transition. The dotted curve is a guide to the eye.

for different L_z's were measured in a single scan. Model calculations which include the pressure dependence of the well width, barrier height, dielectric constant, carrier effective masses, and the excitonic Rydberg have been carried out by two independent groups, who find excellent agreement with the data.[6,7]

In the present study, due to the derivative nature and high sensitivity of the PR spectra, we are able to observe *CnHn* for n up to 7. A difference-energy analysis similar to that performed in Ref. 3 was performed to deduce $\Delta\alpha$, the difference in α between these transitions. Figure 3 shows a plot of $\Delta\alpha$ versus ΔE, where $\Delta\alpha$ is the change in the pressure coefficient and ΔE is the difference in the energy, and both with respect to the $C1H1$ transition. The line through the data is a guide to the eye. A trend similar to that of the well-width dependence of $C1H1$ is evident. Ting and Chang[7] have calculated the change in α with L_z for $n=1-5$. While their calculations does not extend up to $L_z=260$ Å, a decrease in α with increasing n for a given L_z is predicted, and is in qualitative agreement with our results.

While several effects compete to alter α in a MQW structure compared with that of bulk GaAs, the major effect is due to the pressure-induced increase in the electron effective mass m_e^* in the Γ conduction band (CB). Christensen[9] has calculated this effect for bulk GaAs using self-consistent relativistic band model. Beyond 30 kbar, close to the crossover of the Γ and X CB's, this change in m_e^* is nonlinear (see Fig. 11 of Ref. 9). We have used this result to compute the confinement energy ΔE_{Cn} of the nth electronic state in the CB quantum well at a given pressure. The transition energy E_{mn} corresponding to the $CnHm$ transition is

$$E_{mn}(P)=E_g(P)+\Delta E_{Cn}(P)+\Delta E_{Vm} \ .$$

The pressure dependence of the band gap of bulk GaAs is indicated in $E_g(P)$. The confinement energies in the valence-band wells are taken to be independent of pressure.

Figures 4 and 5 show the PR energies as a function of pressure at 300 K. The energies of *CnHn* transitions for $n=1-7$ are shown. We made several model calculations to evaluate the relative importance of competing effects on $E_{mn}(P)$. The confinement energies ΔE_{Cn} and ΔE_{Vm} were computed from a Kronig-Penney model[8] assuming constant values for the electron and hole effective masses at the band extrema.[16] The pressure dependence of the direct band gap of GaAs was taken from the equation

$$E_g(P)=E_g(P=0)+aP+bP^2 \ ,$$

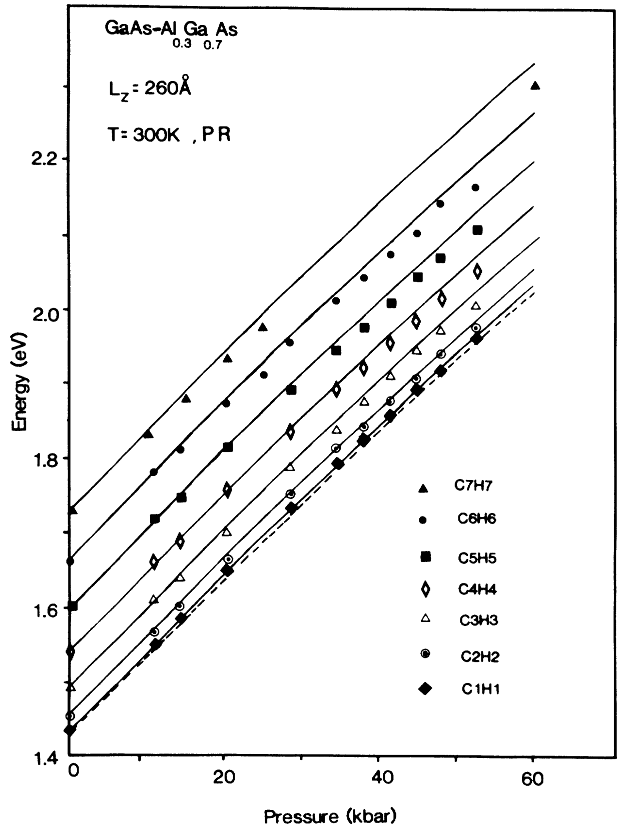

FIG. 4. Pressure dependence of the MQW transition energies at 300 K. The curves passing through the data were calculated from a finite-well model with appropriate band parameters and a constant value for the electron effective mass.

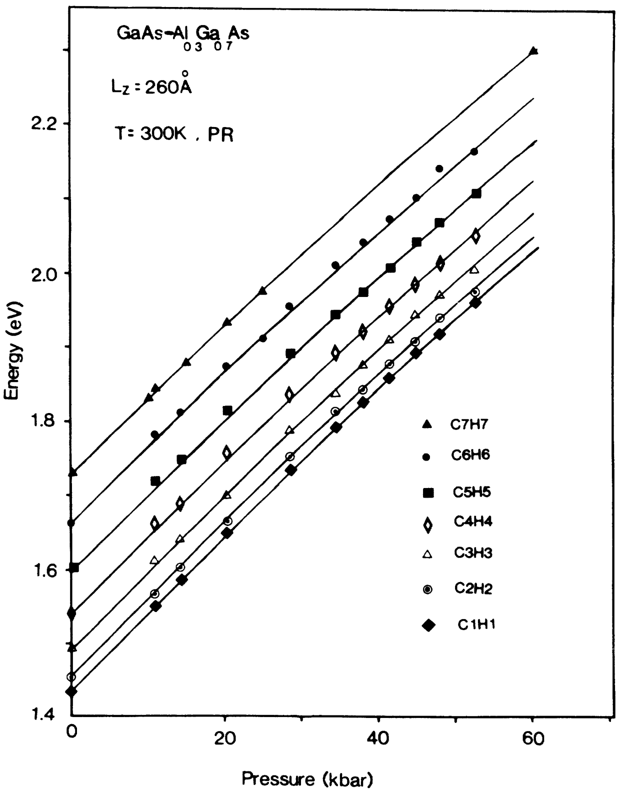

FIG. 5. Same as Fig. 4, except the curves contain the variation of the electron effective mass with pressure as calculated by Christensen. Note the substantially better fit for higher transitions as compared to Fig. 4.

where a and b are the linear and quadratic pressure coefficients and E_g is the band gap at 300 K. We used $a = 11.0$ meV/kbar and $b = -1.6\times10^{-2}$ meV/kbar^2 which are obtained from a linear least-squares fit to the energy of the $C1H1$ transition.[17] Figure 4 shows the result of such a calculation by solid curves. It can be seen that the fit is good for all transitions at low pressures. However, for higher pressures the calculated curve is higher in energy than the data. This difference increases with increasing n.

In Fig. 5 we included the pressure dependence of the electron effective mass from Fig. 11 of Ref. 9 to evaluate ΔE_{Cn}. This leads to a considerable improvement in the fit for the data at higher n and higher pressures. This result is consistent with the conclusions of the more sophisticated theoretical calculations.[6,7]

B. Higher band transitions

It is well known that GaAs the effect of pressure is to move the Γ CB higher in energy at a faster rate than the L band. The X-band minima have a slight negative pressure coefficient. The ordering of the Γ and X bands is reversed beyond ~35 kbar. The L band remains intermediate for most pressures, except for a small range of crossover region. In a MQW, due to the band offset between the well and barrier materials, the energy of the X band of $Al_xGa_{1-x}As$, measured from the top of the valence band of GaAs, is lower in energy than the energy of the X band of GaAs. Staggered transitions from the X band of $Al_xGa_{1-x}As$ to the top of the valence band of GaAs across the heterointerface have been observed in PR and PL under pressure.[1–3,14,18]

Figure 6 shows the PR spectra for pressures beyond the Γ-X crossover. The PR signal decreases drastically as expected. Peak 1 decreases relative to the others and additional peaks upper at lower energies. Figure 7 shows a plot of the pressure dependence of these extra peaks. Only the $C1H1$ transition is shown as a reference. The line passing through the E^x transitions was drawn with its intercept of 1.84 eV corresponding to the energy of the X band of the $Al_{0.3}Ga_{0.7}As$ staggered transition with a conduction- to valence-band offset ratio of 70:30 for the quantum wells.[3,16] The pressure coefficient was taken to be -1.5 ± 0.2 meV/kbar, which is in agreement with our previous result.[1] We identify the transition denoted E^L as being due to the L band in GaAs. The pressure coefficient of this transition is 2.8 ± 0.3 meV/kbar with an energy intercept of 1.71 eV. The peaks denoted $E^{L'}$ seem to originate from the L band of the $Al_{0.3}Ga_{0.7}As$ barrier material. The dashed line in Fig. 7 is drawn with the intercept corresponding to 1.8 eV and a slope of 2.8 meV/kbar. The transitions denoted U are of unknown origin. More information is required to identify them.

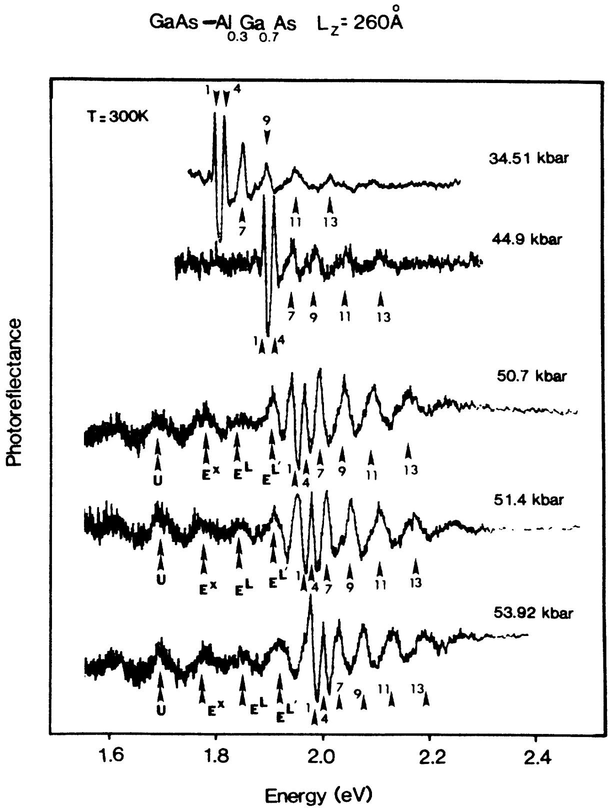

FIG. 6. PR spectra under pressures close to and beyond the Γ-X crossover. Notice the new peaks below peak 1 which appear at higher pressures.

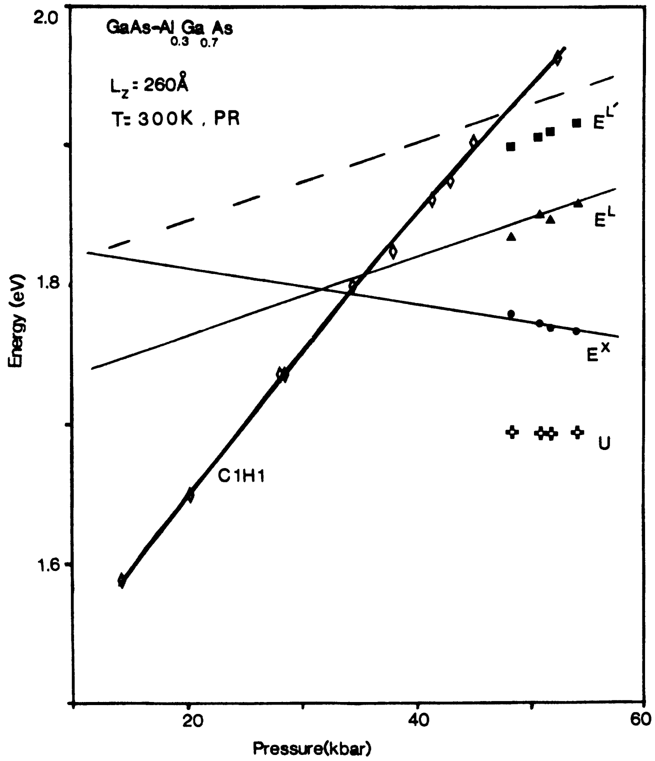

FIG. 7. Pressure dependence of the transitions associated with the L and X bands at 300 K.

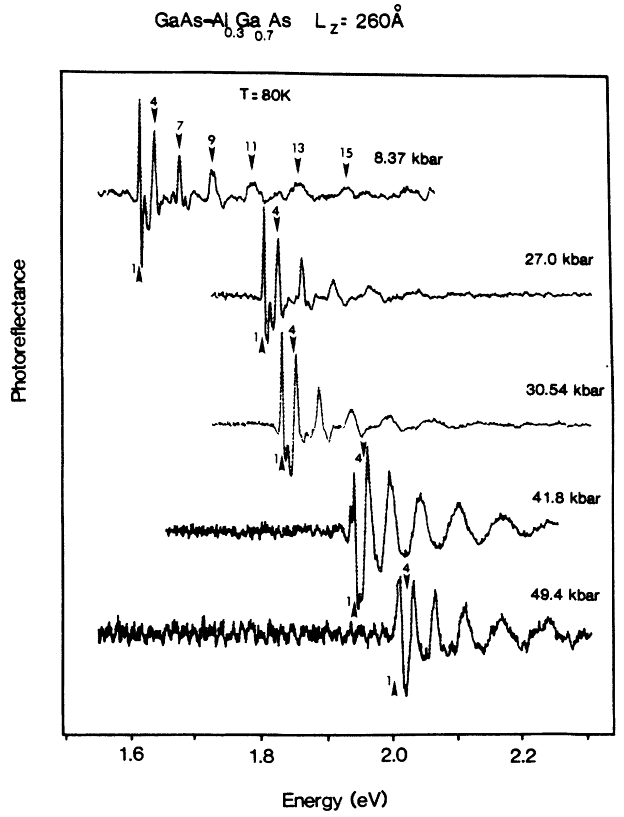

FIG. 8. PR spectra under pressure at 80 K.

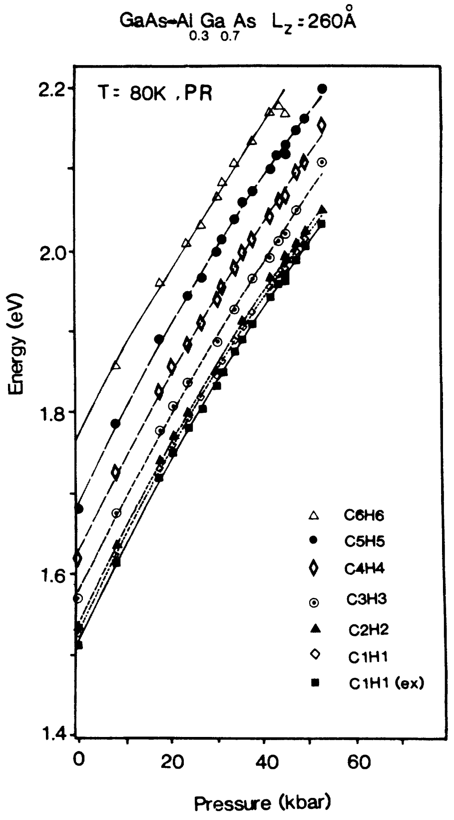

FIG. 9. Pressure dependence of the transition energies. The curves are due to a least-squares fit.

C. Low-temperature studies

Figure 8 shows the pressure evolution of the PR spectra at 80 K. The effect of lowering the temperature is to shift the spectra to a higher energy. The temperature coefficients are found to be the same as that of bulk GaAs and can be fitted to the Varshni equation.[14,16] A considerable sharpening of the $C1H1$ transition enables one to identify the 1*s* and band-to-band transition of the $C1H1$ exciton (see Fig. 1 and Table I). The effect of pressure is to move the train of Γ-band transitions to higher energies. As the Γ-X crossover is reached, the transitions weaken in intensity and become broader, as is seen in Fig. 8.

Figure 9 shows the pressure dependence of the energies with the lines passing through them due to nonlinear least-squares fits. The pressure dependence is identical to that found at the room temperature. The model calculation which fits the data in Fig. 5 is found to describe accurately the data in Fig. 9 when the energies are corrected for the temperature shift by the Varshni equation,

$$E(T)=E(T_0)+\frac{\alpha' T_0^2}{\beta'+T_0}-\frac{\alpha' T^2}{\beta'+T} ,$$

where the energy at temperature T is related to that at T_0. α' and β' are the Varshni coefficients given by 5.41×10^{-4} eV/K and 204 K, respectively.[11,17] Hence we believe that the effects due to quantum confinement are independent of temperature, within experimental error.

IV. CONCLUSIONS

A comprehensive study of a large number of MQW transitions under pressure has yielded a quantitative understanding of the effect of carrier confinement. To our knowledge this is the first study of the photoreflectance spectra under high pressures and at low temperatures. A model calculation which includes the pressure dependence of the electron effective mass describes the data accurately. Transitions associated with higher band extrema have been observed and their pressure coefficients deduced.

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[1] A. Kangarlu, H. R. Chandrasekhar, M. Chandrasekhar, F. A. Chambers, B. A. Vojak, and J. M. Meese, Superlattices Microstruct. **2**, 563 (1986); in *Proceedings of the 18th International Conference on the Physics of Semiconductors, Stockholm, 1986,* edited by O. Engström (World Scientific, Singapore, 1987), p. 569.

[2] U, Venkateswaran, M. Chandrasekhar, H. R. Chandrasekhar, T. Wolfram, R. Fischer, W. T. Masselink, and H. Morkoç, Phys. Rev. B **31**, 4106 (1985).

[3] U. Venkateswaran, M. Chandrasekhar, H. R. Chandrasekhar, B. A. Vojak, F. A. Chambers, and J. M. Meese, Phys. Rev. B **33**, 8416 (1986); in *Proceedings of the 18th International Conferences on the Physics of Semiconductors, Stockholm, 1986,* Ref. 1, p. 621.

[4] A. Kangarlu, Ph.D. thesis, University of Missouri–Columbia, 1987 (unpublished).

[5] U. Venkateswaran, Ph.D. thesis, University of Missouri–Columbia, 1985 (unpublished).

[6] P. Lefebvre, B. Gil, and H. Mattieu, Phys. Rev. B **35**, 5630 (1987); see the references in this paper for alist of related publications on this subject.

[7] D.Z.-Y. Ting and Y. C. Chang, Bull. Am. Phys. Soc. **32**, 760 (1987); Phys. Rev. B **36**, 4359 (1987).

[8] A. Kangarlu, Y. M. Kapoor, H. R. Chandrasekhar, and Meera Chandrasekhar, Trans. Miss. Acad. Sci. **20**, 73 (1986).

[9] N. E. Christensen, Phys. Rev. B **30**, 5753 (1984).

[10] J. L. Shay, Phys. Rev. B **2**, 803 (1970).

[11] A. Kangarlu, H. R. Chandrasekhar, M. Chandrasekhar, Y. M. Kapoor, B. A. Vojak, F. A. Chambers, and J. M. Meese, Phys. Rev. B **37**, 1035 (1988).

[12] W. T. Masselink, P. J. Pearah, J. Klem, C. K. Peng, H. Morkoç, G. D. Sanders, and Y. C. Chang, Phys. Rev. B **32**, 8027 (1985); R. C. Miller, A. C. Gossard, G. D. Sanders, and Y. C. Chang, *ibid.* **32**, 8452 (1985); G. D. Sanders and Y. C. Chang, *ibid.* **35**, 1300 (1987); **32**, 5517 (1985).

[13] R. C. Miller, D. A. Kleinman, W. T. Isang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981); M. H. Meynadier, C. Delalannde, G. Bastard, M. Woos, F. Alexander, and J. L. Lievin, *ibid.* **31**, 5539 (1985); D. Dawson, K. J. Moore, G. Duggan, H. I. Ralph, and C. T. B. Foxon, *ibid.* **34**, 6007 (1986); E. S. Koteles and J. Y. Chi, SPIE Int. Soc. Opt. Eng. (to be published)

[14] H. Shen, X. C. Shen, F. H. Pollak, and R. N. Sacks, Phys. Rev. B **36**, 3487 (1987).

[15] D. E. Aspnes, in *Handbook of Semiconductors,* edited by T. S. Moss (North-Holland, New York, 1980), p. 109.

[16] S. Adachi, J. App. Phys. **58**, R1 (1985).

[17] In this relatively wide well sample, the confinement energy of $n=1$ is ~ 10 meV, and its pressure variation is very small. Hence a and b are close to that of bulk GaAs, within experimental error.

[18] D. J. Wolford, in *Proceedings of the 18th International Conference on the Physics of Semiconductors, Stockholm, 1986,* Ref. 1, p. 1115.