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Phonon coupling and X-Γ mixing in GaAs-AlAs short-period superlattices

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An investigation of phonon satellites (PS) of excitonic recombination, and photoluminescence decay times, in a GaAs-AlAs superlattice under hydrostatic pressures up to 50 kbar is reported. Beyond the X-Γ crossover it is shown that the PS are momentum conserving, and that the phonon scattering processes and the X-Γ mixing leading to finite oscillator strength in the zero phonon line both proceed predominantly via coupling with the same Γ state.

Indirect exciton, type-II superlattice (SL) behavior in the GaAs-AlAs system has been observed recently.[1-6] In a type-II SL electrons and holes are spatially separated, and are localized predominantly in the AlAs and GaAs layers, respectively. This contrasts with a type-I SL where both carriers are localized in the GaAs layers. For GaAs widths less than 35 Å the lowest GaAs-related Γ state occurs at energies above the X state in the indirect gap AlAs,[3,7] and a type-II SL, indirect in real and k-space results. A transition from type-I to type-II behavior in wide $GaAs$-$Ga_xAl_{1-x}As$ quantum wells (QW's) can also be achieved by application of hydrostatic pressure[8] or electric field.[7] A characteristic feature of an indirect-gap SL is that momentum conserving (MC) phonon satellites (PS) of the excitonic recombination are observed.[1,3,6] Finite oscillator strength in the zero-phonon line (ZPL) can arise from zone-folding effects of the X point electron states to $k=0$, or from X-Γ mixing due to disorder at the GaAs-AlAs interface.

In the present work, a study of the phonon coupling in the photoluminescence (PL) spectrum of a GaAs-AlAs SL as a function of hydrostatic pressure (P) up to 50 kbar is reported. These high pressures strongly perturb the SL band structure, enabling firm conclusions to be reached as to the identity of the intermediate virtual state in the MC phonon scattering process. Time decay measurements are also performed to study directly the variation of the oscillator strength of the lowest X state with X-Γ separation.

The experiments were carried out on an undoped GaAs-AlAs SL structure with GaAs width of 12 monolayers (ML, 1 ML = 2.83 Å) and AlAs width of 8 ML. The sample, grown by molecular-beam epitaxy, consisted of a 1.0-μm thick GaAs buffer layer, followed by 100 repeats of the (12,8) SL, capped by 240 Å of GaAs.[6] The high-pressure experiments on 100-μm^2 area, 35-μm-thick samples were carried out at 2 K in argon loaded, diamond anvil cells (DAC),[9] with a small chip of ruby for pressure calibration. PL was excited using the 4880-Å line of an Ar^+ laser, dispersed with a 0.75-m spectrometer and detected by a GaAs photomultiplier. For time decay measurements, excitation pulses of 50 nsec to 1 μsec duration (peak power density $I_{exc} \approx 10$ W/cm^2) were obtained from the Ar^+ laser using an acousto-optic modulator. PL transients were analyzed by a boxcar integrator. The time response of the system was ~50 nsec, an order of magnitude less than the minimum PL decay time.

PL spectra (2 K) as a function of P are shown in Fig. 1. At $P=0$ [Fig. 1(a)], the spectrum is composed of an exciton ZPL [$E_{1h}(\Gamma)$] and a PS 36.7 meV lower in energy, very close to the Γ-point LO phonon energy of GaAs.[6] The Stokes' shift between PL and PL excitation at $P=0$ is 7.5 meV,[6] typical for a type-I direct-gap SL. The LO phonon satellite arises from in-plane exciton localization, which enhances the strength of exciton-LO phonon coupling.[10] As the excitation intensity is increased and the more localized exciton states are saturated, the relative intensity of the PS to the ZPL is observed to decrease strongly.

At the lowest pressure [2.4 kbar, Fig. 1(b)], the form of the PS is very different. Three PS are observed (labeled Y_1, Y_2, and Y_3) below the ZPL [$E_{1h}(X)$]. The overall character of the PS remains the same up to 50 kbar, although there is an increase of ~5% in all the phonon energies. At 3.3 kbar, the Y_1, Y_2, and Y_3 energies are 27.8, 35.1, and 48.5 meV, respectively, close to those reported for an indirect gap (10,11)ML GaAs-AlAs SL,[1] and for an (11,8)ML structure.[6] The Y_1 satellite is ascribed to a zone boundary, MC LA(X) phonon[1,6] since it is close in energy to the LA(X) energies of AlAs and GaAs.[1,6] The Y_2 and Y_3 satellites fall in the range of the optic-phonon branches of GaAs and AlAs, respectively, but due to the small optic-phonon dispersion they cannot be attributed unambiguously to Γ or X point phonons on this evidence alone.[1,6,11] The coupling to the Y_1 LA(X) phonon and the Y_3 AlAs optic phonon shows that crossover to an indirect gap type-II SL, with X-derived electron state lowest in energy, has occurred between 0 and 2.4 kbar. This is supported by the detection of a weak Γ-related PL peak [$E_{1h}(\Gamma)$] to higher energy than $E_{1h}(X)$ [Fig. 1(b)].[12] The X and Γ transition energies are plotted as a function of P in Fig. 2. Pressure coefficients $dE_\Gamma/dP = +10.3$ meV/kbar and $dE_X/dP = -2.1$ meV/kbar are deduced. These compare with reported values of $dE_\Gamma/dP = +10.7$ and $dE_X/dP = -1.3$ meV/kbar for bulk GaAs,[13] and $dE_X/dP = -2.4$ meV/kbar for a GaAs-AlAs SL.[14] Extrapolation of the Γ and X energies in Fig. 2 to $P=0$ leads to the conclusion that the Γ,X states are within ± 2 meV of one another at $P=0$, consistent with the type-I nature

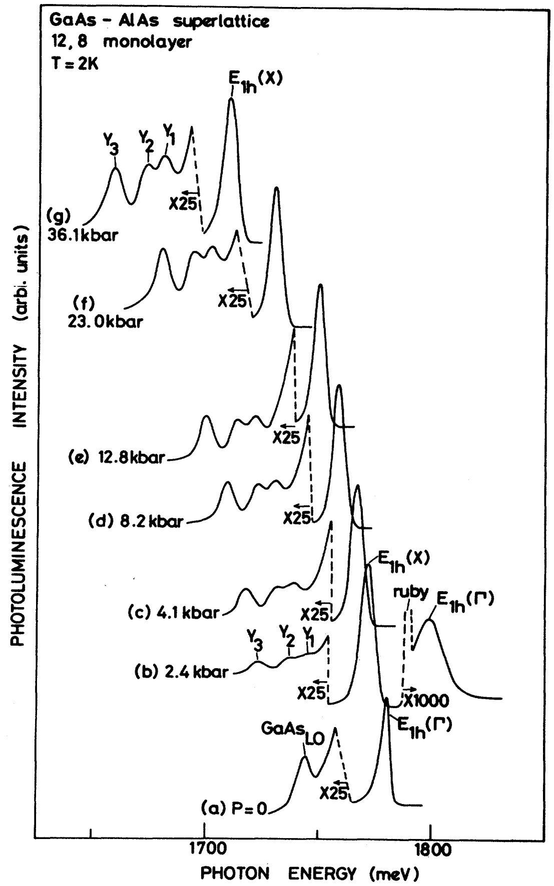

FIG. 1. 2-K PL spectra from $P=0$ to 36.1 kbar. At $P=0$ [Fig. 1(a)] the SL has a direct gap, and replication of $E_{1h}(\Gamma)$ by the GaAs LO(Γ) phonon is observed. For all finite pressures [Figs. 1(b)–1(g)], the SL is indirect. Coupling to three MC phonons, Y_1, Y_2, and Y_3 is observed. The increase in $I(Y_n)/I[E_{1h}(X)]$ with P is clearly seen. Figure 1(a) is obtained in the low power limit at $I_{exc}\sim 0.1$ W/cm^2, Figs. 1(b)–1(g) at 10 W/cm^2. For $I_{exc}=10$ W/cm^2, $I[\mathrm{LO}(\Gamma)]/I[E_{1h}(\Gamma)]$ at $P=0$ is only 0.03% [1.1% at 0.1 W/cm^2 in Fig. 1(a)], as compared to the ratio R_2 for the Y_2[LO(X)] MC satellite of 0.1% at 2.4 kbar [Fig. 1(b)] and 10 W/cm^2.

of the SL at $P=0$.

We now turn to the intensity ratio (R_n) of the PS(Y_n) to the ZPL, and its dependence on P (Fig. 3). $R_3(P)$ is plotted, but similar results are obtained for $R_1(P)$ and $R_2(P)$. The most striking result is that $R_3(P)$ increases rapidly up to 15 kbar, but then nearly saturates at a value of $\sim$1.4–1.5% for $P>20$ kbar. This result can be understood if the mixing mechanism which gives oscillator strength to the ZPL, and the MC phonon scattering process, proceed via the same Γ intermediate state.

The matrix element for electric dipole transitions between conduction and valence bands is given by $M_{c,v} = \langle \psi_c | p | \psi_v^\Gamma \rangle$, where ψ_c and ψ_v^Γ are wave functions at the conduction and valence-band extrema and p is the dipole operator. $M_{c,v}$ is only nonzero if $|\psi_c\rangle$ contains Γ-wave-function character. Within first-order perturbation theory for Γ-X mixing by a potential V, the matrix element becomes

$$M_{c,v} = \frac{\langle \psi_c^X | V | \psi_c^\Gamma \rangle \langle \psi_c^\Gamma | p | \psi_v^\Gamma \rangle}{E_\Gamma - E_X} . \quad (1)$$

Mixing with the lowest confined Γ state (Γ_1) only has been included. The oscillator strength for radiative transi-

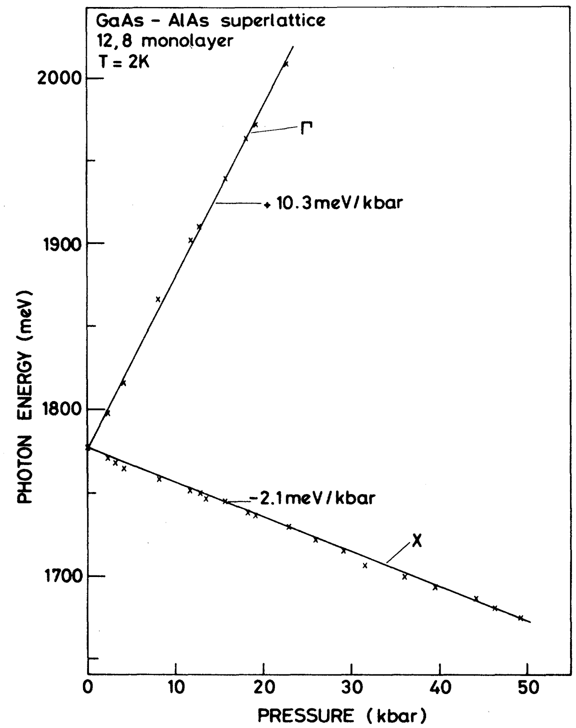

FIG. 2. X and Γ transition energies as a function of P. $E_{1h}(\Gamma)$ is only observable up to 23 kbar.

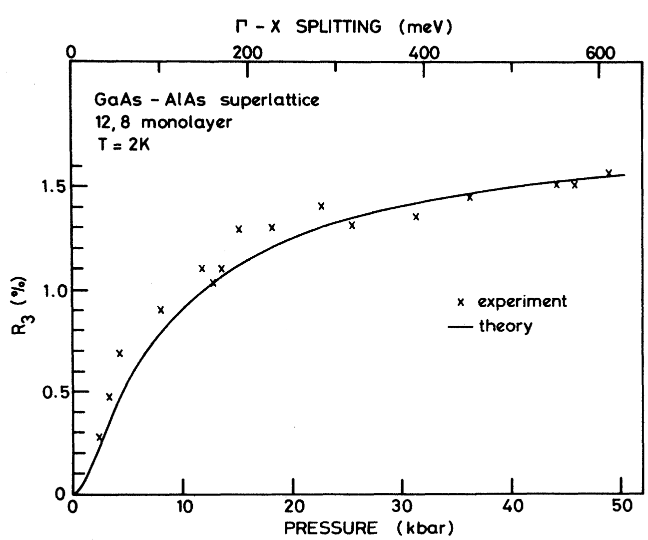

FIG. 3. $R_3(P)$, the ratio of the intensity of the Y_3 phonon satellite to the intensity of the ZPL as a function of P: $\times$, experimental points; solid line, fit to $[\Delta/(\Delta+\hbar\omega_{ph})]^2$.

tions is proportional to the square of the matrix element $[M_{c,v}^2 \propto 1/\Delta^2$ where Δ is the Γ-X splitting $(E_\Gamma - E_X)]$.

For MC phonon-assisted PL transitions, the analysis is similar, with

$$M_{c,v}^{\mathrm{ph}} = \frac{\langle \psi_c^X | H_{e\text{-ph}} | \psi_c^\Gamma \rangle \langle \psi_c^\Gamma | p | \psi_v^\Gamma \rangle}{(E_\Gamma + \hbar\omega_{\mathrm{ph}}) - E_X} , \quad (2)$$

where $H_{e\text{-ph}}$ is the electron-phonon interaction Hamiltonian, phonon scattering only through the Γ_1 virtual, intermediate state has been included, and $\hbar\omega_{\mathrm{ph}}$ is the phonon energy. The term $(E_\Gamma + \hbar\omega_{\mathrm{ph}})$ is the energy of the virtual state. The oscillator strength is proportional to $(M_{c,v}^{\mathrm{ph}})^2$ and hence to $1/(\Delta + \hbar\omega_{\mathrm{ph}})^2$, and the PS fractional intensity R_n is proportional to $[\Delta/(\Delta + \hbar\omega_{\mathrm{ph}})]^2$.[15] The other terms in Eqs. (1) and (2) are difficult to determine quantitatively, but to a good approximation they are pressure independent. The pressure dependence of $[\Delta/(\Delta + \hbar\omega_{\mathrm{ph}})]^2$ is plotted as the solid line on Fig. 3, using the variation of Δ with P from Fig. 2. A good fit to the observed variation of $R_3(P)$ is obtained (normalized to fit the value of R_3 at high P). The initial rapid increase of R_3 with P, as well as the near saturation above 20 kbar when $\Delta \gg \hbar\omega_{\mathrm{ph}}$, are well accounted for, showing that Y_3 is a symmetry-breaking MC phonon satellite. The form of the variation of R_3 and P arises since at low P the ZPL has relatively high oscillator strength since Γ, X are nearly in resonance $[E_\Gamma$-$E_X \approx 0$ in Eq. (1)], whereas the intermediate state for the PS is out of resonance at $\hbar\omega_{\mathrm{ph}}$ higher in energy $[E_\Gamma + \hbar\omega_{\mathrm{ph}} - E_X \neq 0$ in Eq. (2)]. Thus at low P, small values of the ratio R will be expected. At high P, very little variation of R_3 with P will occur since both the zero phonon and MC phonon satellite processes involve scattering through an intermediate state, which is relatively far away in energy at $\Delta \gg \hbar\omega_{\mathrm{ph}}$.

The variation of the relative intensities of all three PS with P is very similar, showing that they are all momentum conserving, and that they all scatter through the same Γ_1 intermediate state. This result differs from that predicted group theoretically for bulk AlAs or GaAs where only LO(X) scattering through Γ_1 is allowed.[16] However, a similar calculation in the D_{2d} SL symmetry shows that X-Γ scattering by LA(X) and LO(X) is allowed, consistent with the attribution of $Y_1 \equiv$ LA(X), $Y_2 \equiv$ LO(X), $Y_3 \equiv$ LO(X). The fact that Y_n are MC satellites is further supported by the power independence of the ratios R_n over two orders of magnitude of excitation intensity, in contrast to the saturation of the localization-induced LO(Γ) phonon at $P=0$.

Further information on the variation of $M_{c,v}$ with P is obtained from PL lifetime (τ_{PL}) measurements, since the radiative decay rate $1/\tau_R$ is proportional to $M_{c,v}^2$ when zero-phonon transitions are dominant, as in the present sample. The variation of τ_{PL} with P is shown in Fig. 4. The PL decays with detection set at the peak of $E_{1h}(X)$ are single exponentials over one and a half orders of magnitude (see inset). The observation of single exponentials[17] is in agreement with recent results of Dawson *et al.*,[18] but does not agree with earlier results,[1-3] where the contribution from random Γ-X mixing may have been greater. A strong increase in τ_{PL} with P is observed, from ~400 nsec and 3 kbar to ~12 μsec at 36 kbar. This

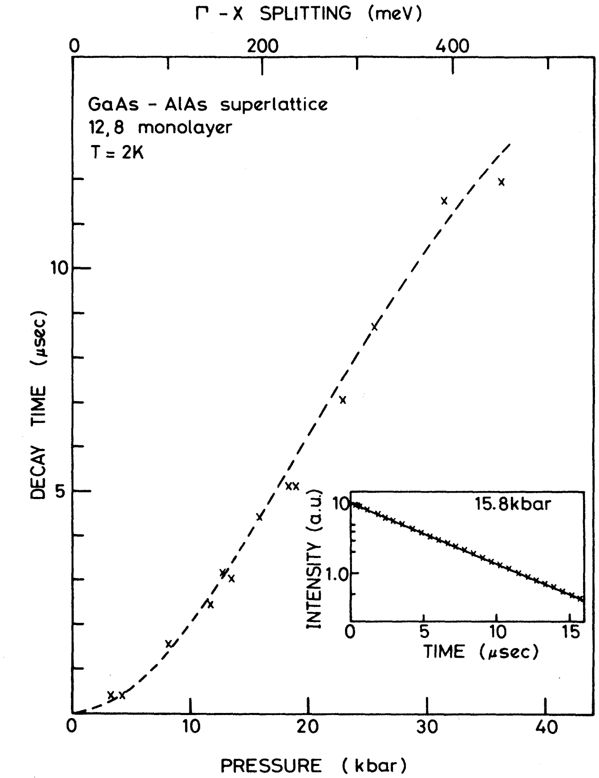

FIG. 4. τ_{PL} as a function of P at 2 K. ×, experiment; dashed line, fit to $\tau_{\mathrm{PL}} = \tau_R \tau_{NR}/(\tau_R + \tau_{NR})$ with $\tau_R \propto \Delta^2$ and $\tau_{NR} = 22$ μsec. The small increase in τ_{PL} between 31 and 36 kbar *may* indicate the increased importance of nonradiative processes at 36 kbar. The inset shows a PL decay curve at 15.8 kbar.

shows clearly that mixing between the lowest X and Γ states is the dominant mechanism which provides oscillator strength for the decay of the X-point excitons. However, above 15 kbar the rate of increase of τ_{PL} with P is slower than the quadratic behavior expected from Eq. (1) $(\tau_R \propto M_{c,v}^{-2} \propto \Delta^2)$.

The departure from quadratic behavior may arrive due to the contribution from nonradiative processes (rate τ_{NR}^{-1}) which will lead to a decrease of the PL decay times; they will have a relatively larger effect at long τ_R since $\tau_{\mathrm{PL}}^{-1} = \tau_R^{-1} + \tau_{\mathrm{NR}}^{-1}$. The observed variation of τ_{PL} can be explained reasonably well if τ_R is proportional to P^2, and $\tau_{\mathrm{NR}} = 22$ μsec, as shown by the dashed line on Fig. 4. An upper limit of ~2 to any change in PL quantum efficiency from 3 to 30 kbar was found, consistent with $\tau_{\mathrm{NR}} \gtrsim 20$ μsec. The occurrence of nonradiative processes will not affect the Δ dependence of the $R_n(\Delta)$ analysis presented earlier.

Dawson *et al.*[18] have made a comparison of τ_{PL} values at $P=0$ in three separate GaAs-AlAs SL's. They find good agreement with the variation of τ_R vs Δ^2 predicted by Eq. (1), so long as the change in envelope function overlap integral between the samples is included.[19] In such studies, the possible effects of band-gap variations with P on τ_R are avoided, but in contrast to experiments as a function of P on the same sample, it may be difficult to eliminate the effects of sample to sample variation in the τ vs Δ analysis.[20]

In conclusion, the nature of the phonon coupling and X-Γ mixing in a GaAs-AlAs superlattice have been studied as a function of hydrostatic pressure. The principal results are that all the PS are momentum conserving, and that the phonon coupling and the zero phonon X-Γ mixing both proceed via scattering through the same Γ intermediate state.

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[12]For $P > 0, E_{1h}(\Gamma)$ has 3.3 times greater width than $E_{1h}(X)$ [Fig. 1(b)]. This is due either to the Γ-X scattering rate ($\tau_{\Gamma\text{-}X}^{-1}$) being very much faster than the electron cooling rate by acoustic phonon emission in Γ, or to lifetime broadening for electrons at Γ (~ 10 meV expected for $\tau_{\Gamma\text{-}X}^{-1}$ of 0.1 psec). At $P=0$ [Fig. 1(a)], when Γ is close in energy to X, the $E_{1h}(\Gamma)$ width (5.1 meV) is very similar to that found for $E_{1h}(X)$ in Figs. 1(b)-1(g).

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[19]The variation of τ_{PL} vs Δ was also studied in Ref. 7. By comparing with the τ vs Δ^2 relation they concluded that the Γ-X mixing potential was less strong at long SL periods.

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