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Pressure-tuned resonance Raman scattering and photoluminescence studies on MBE grown bulk GaAs at the E_0 gap

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Abstract. Hydrostatic pressure has been used to tune in resonance Raman scattering (RRS) in bulk GaAs. Using a diamond anvil cell, both the photoluminescence peak (PL) and the 2 LO and LO-phonon Raman scattered intensities have been monitored, to establish RRS conditions. When the E_0 gap of GaAs matches $\hbar\omega_S$ or $\hbar\omega_L$, the 2 LO and LO-phonon intensity, respectively, exhibit resonance Raman scattering maxima, at pressures determined by $\hbar\omega_L$. With 647·1 nm radiation ($\hbar\omega_L = 1{\cdot}916\,\text{eV}$), a sharp and narrow resonance peak at 3·75 GPa is observed for the 2 LO-phonon. At this pressure the 2 LO-phonon goes through its maximum intensity, and falls right on top of the PL peak, revealing that $\hbar\omega_S(2\,\text{LO}) = E_0$. This is the condition for "outgoing" resonance. Experiments with other excitation energies ($\hbar\omega_L$) show, that the 2 LO resonance peak-pressure moves to higher pressure with increasing $\hbar\omega_L$, and the shift follows precisely the E_0 gap. Thus, the 2 LO RRS is an excellent probe to follow the E_0 gap, far beyond the Γ-X cross-over point. A brief discussion of the theoretical expression for resonance Raman cross section is given, and from this the possibility of a double resonance condition for the observed 2 LO resonance is suggested. The LO-phonon resonance occurs at a pressure when $\hbar\omega_L \approx E_0$, but the pressure-induced transparency of the GaAs masks the true resonance profile.

Keywords. Pressure-tuning; resonance Raman scattering; semiconductors.

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1. Introduction

In resonance Raman scattering (RRS) experiments (Cardona 1982) it is customary to vary the Raman excitation frequency ($\hbar\omega_L$) while the electronic gap energies of the system under study is kept constant. However, it is possible to pressure-tune the electronic gap energies of the material into resonance with a fixed Raman excitation frequency ($\hbar\omega_L$), and observe RRS (Trömmer *et al* 1976; Trömmer and Cardona 1978; Yu and Welber 1978; Holtz *et al* 1989; Aoki *et al* 1984). This method is particularly suited for zinc-blende type semiconductors, since their direct gaps (E_0) have large pressure coefficients ($\sim 100\,\text{meV/GPa}$). Although GaAs is one of the most extensively studied semiconductors from the point of view of RRS, pressure-induced RRS experiments in bulk GaAs have received cursory attention only.

While carrying out pressure-induced RRS experiments in InGaAs/AlGaAs strained layer multiple quantum well (MQW) structures on GaAs substrates, we encountered a serious interference problem, both in Raman scattering and in photoluminescence

(PL), from the GaAs substrate layer. With increasing pressure, the layers become transparent to the exciting laser frequency, especially when the latter lies in the red region, and the substrate layer of GaAs dominates the Raman features. This prompted us to investigate the pressure-induced RRS of high quality bulk GaAs, and to follow the photoluminescence peak, concurrently. The study has revealed a number of interesting new features concerning the interrelationship between electronic structure, luminescence and RRS in bulk GaAs. These results will be presented and discussed in this paper.

2. Experiments

High quality epitaxial GaAs was grown by molecular beam epitaxy on a (100) substrate of GaAs. The epitaxial layer was 12 μm thick. For pressure experiments, the substrate side was thinned down such that the total sample thickness was brought down to 20 μm. Rectangular pieces of about 100 μm in linear dimension were then cleaved, and were mounted inside the gasket hole of the diamond cell.

Hydrostatic pressure was generated using the gasketed Mao-Bell type (Jayaraman 1983) diamond anvil cell, with argon as the pressure medium. High pressure argon filling was carried out using a high pressure gas loading system (Mills *et al* 1980). The pressure generated was calibrated by the well-known ruby fluorescence technique (Barnett *et al* 1973). In some experiments methanol-ethanol was also employed as a pressure medium.

Both Raman and luminescence measurements were carried out at room temperature, with a Spex double monochromator equipped with a conventional photon counting system. For excitation, the 647·1 nm line of the krypton laser was used. This radiation proved to be the best, for the RRS maxima occur in a pressure range well within the hydrostatic limit even when methanol-ethanol was employed as the pressure medium. That the medium should be hydrostatic is an essential requirement for these experiments. The E_0 luminescence peak of GaAs was followed as a function of pressure up to 4·5 GPa. For recording these peaks, the wave number scale was set at 50 cm^{-1}/cm, while for Raman measurements, it was set at 10 cm^{-1}/cm.

The samples were (100) slabs and the scattering geometry was close to the backscattering configuration. In the pressure experiments, the polarization of the incident light could not be set as desired, because of the difficulty in exactly orienting the samples, and the unknown stress birefringence of the anvil diamond. With the (100) slab and backscattering geometry, the TO phonon is normally forbidden.

In figure 1, the 2 LO and LO peaks of GaAs recorded with 647·1 nm excitation are shown for ambient pressure and three other pressures. The 2 LO peak intensity goes through a pronounced maximum near 3·7 GPa due to pressure-induced RRS. The LO peak intensity also rises sharply between 4 and 5 GPa but a distinct maximum is not seen; at higher pressures (not shown) the LO phonon intensity decreases only by a small factor. The 2 LO and LO peak intensities are plotted as a function of pressure in figures 2 and 3 to show their pressure-induced RRS behavior.

In figure 4 (center a, b, c), the photoluminescence peaks recorded at three different pressures near the 2 LO resonance are shown. The peaks are well defined, and correspond to the E_0 gap energy. The sharp spikes riding on the PL peaks are due to

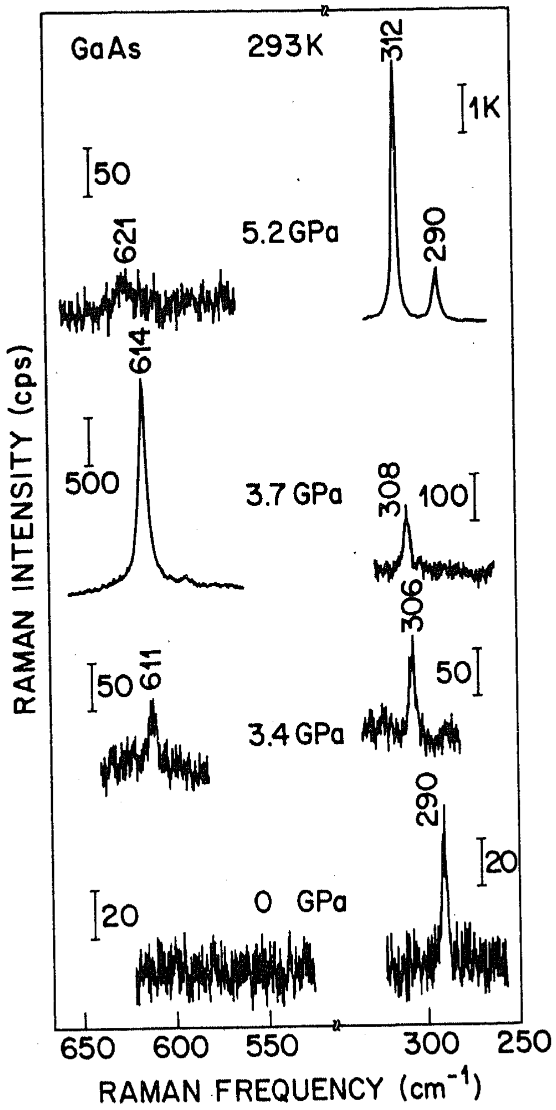

Figure 1. Raman intensity of the 2 LO-phonon (left) and the LO-phonon (right) of bulk GaAs at four different pressures, recorded with the 647·1 nm line of the krypton laser at a power level of 20 mW. Scale for Raman intensities is given in each spectrum. The 2 LO-phonon intensity maximum occurs at 3·75 GPa. The strong narrow peak in the 5·2 GPa spectrum is the LO-phonon (312 cm^{-1}) and the weaker one on the right side (290 cm^{-1}) is the TO mode. The TO begins to appear near resonance and is present in all spectra where LO is strong.

the 2 LO phonon which becomes quite strong; it is, in fact, an order of magnitude stronger than the LO phonon. At 3·75 GPa (see figure 4 marked c) the luminescence is strong, and on this scale the LO phonon is hardly noticeable. The 2 LO phonon sits right on top of the PL peak, and in this situation its intensity has the maximum value. In figure 4(b), a pressure increase of about half a kilobar has moved the PL peak to higher energy relative to the 2 LO peak, and the intensity of the latter has dropped by a factor of two. At 4 GPa (shown in figure 4a) the luminescence peak has shifted further to higher energy relative to the 2 LO, and now, both 2 LO and LO phonon peaks can be seen riding on either side of the PL peak. The intensity of the 2 LO has decreased further and is about a fourth, compared to the value at resonance. On the

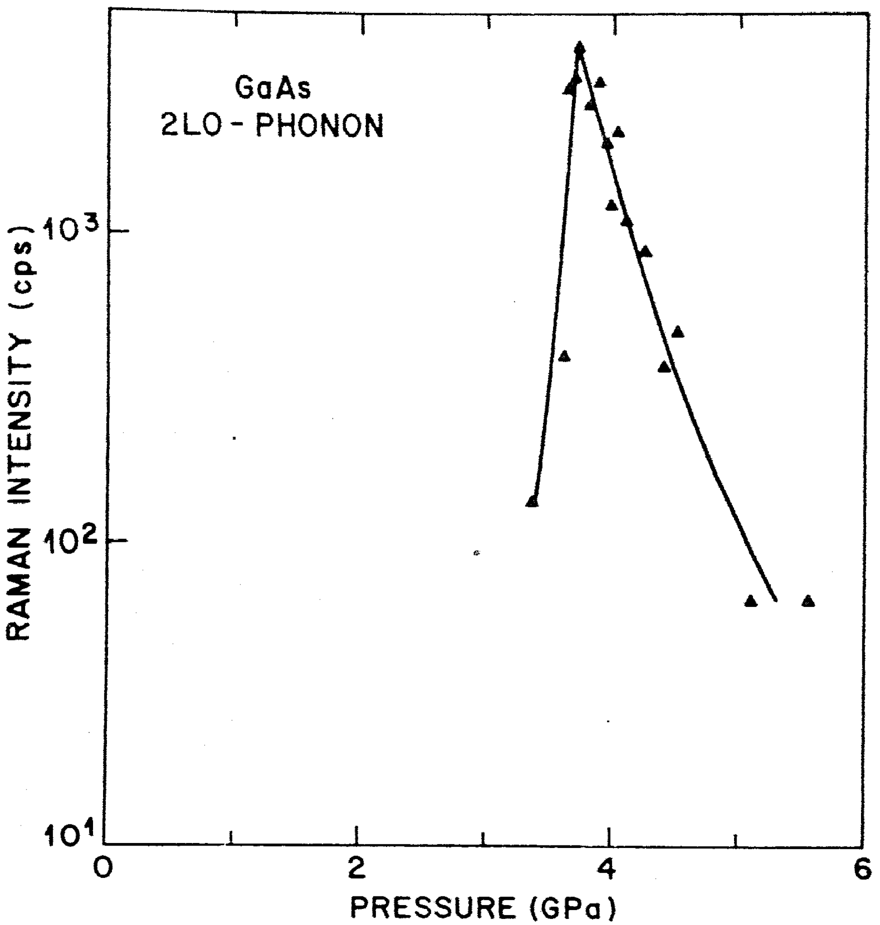

Figure 2. Pressure versus the 2-LO intensity recorded with the 647·1 nm line, at a constant power level of 20 mW. The Raman intensity peaks at 3·75 GPa.

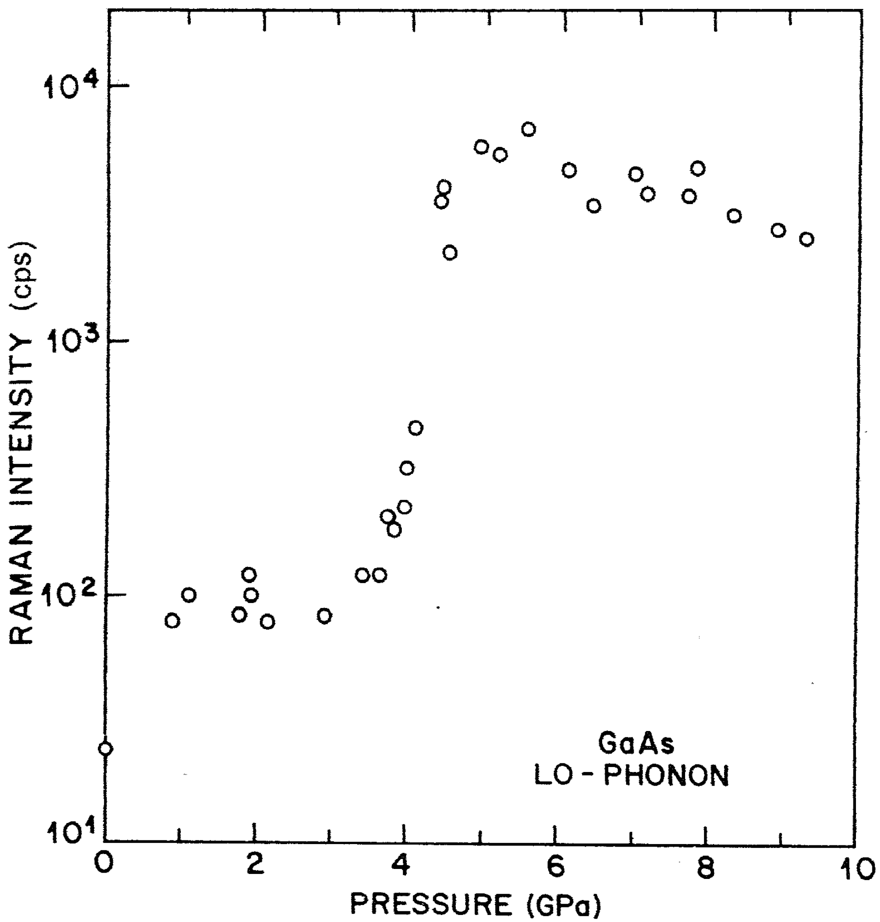

Figure 3. Pressure versus the LO-phonon intensity. The resonance is very asymmetric due to the pressure-induced transparency in GaAs. Pressure-induced transparency masks the true resonance profile in thick samples.

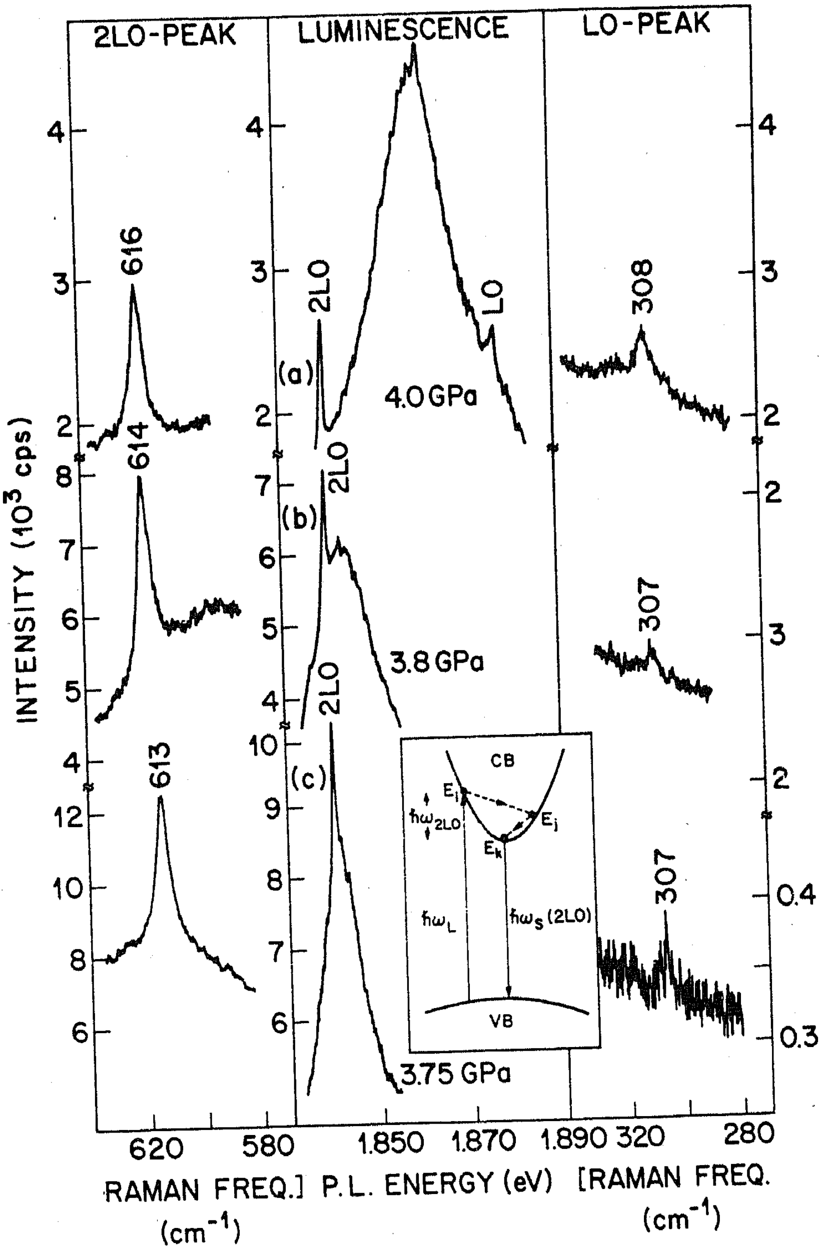

Figure 4. The photoluminescence (PL) peak (center) and the Raman peaks of bulk GaAs in a composite setting, at three different pressures close to the 2 LO resonance, recorded with the 647·1 nm excitation. The spikes on the PL peaks in (b) and (c) are the 2 LO phonon. In (a) the 2 LO and LO are symmetrically situated on either side of the PL peak. The 2 LO peak falls right on top of the PL peak in (c), at the 2 LO resonance while (a) and (b) are slightly away from resonance. The inset to (c) shows the resonant Raman process appropriate to (c) (see text for explanation).

left and right-side in figure 4 the corresponding 2 LO and the LO phonon peaks, respectively, are shown on an expanded wave number scale. At higher pressures, the luminescence peak shifts to higher energy and ultimately vanishes when $E_0 = \hbar\omega_L$ or when Γ crosses X. Concurrently, the 2 LO scattering becomes very weak, while the LO gains enormously in intensity.

Figure 5 is the key diagram to understand pressure-tuned RRS. In the figure the

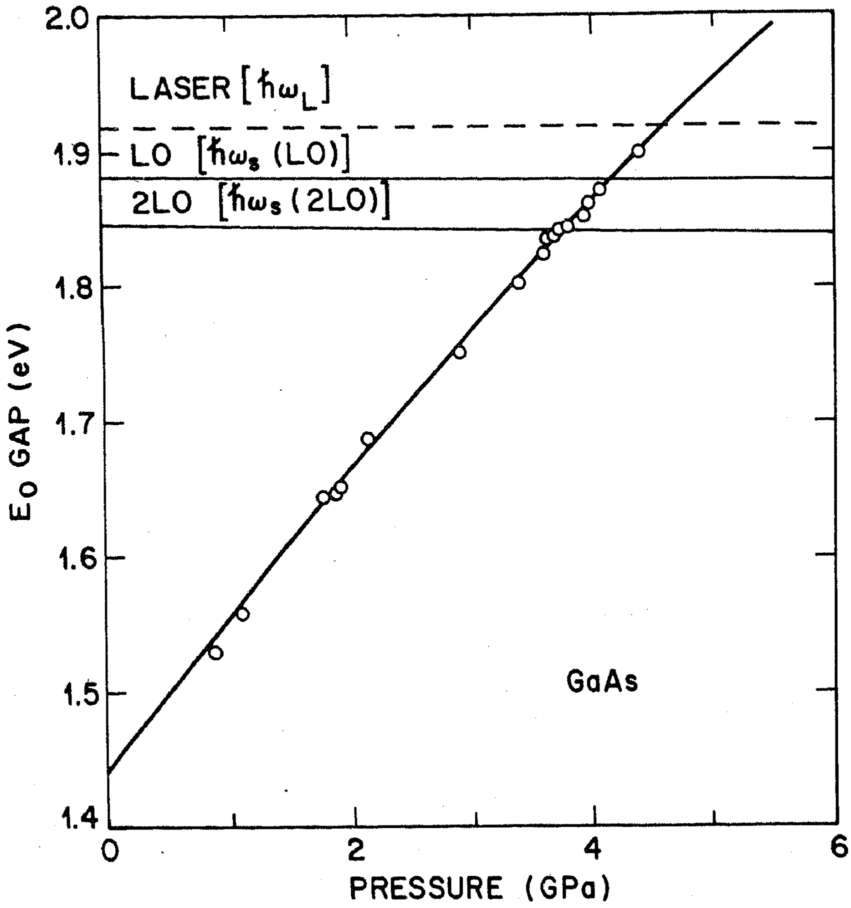

Figure 5. The direct gap (E_0) change with pressure was obtained from the well defined PL peaks. The solid line is a second degree polynomial fit to the data. The three horizontal lines are, respectively, the laser excitation energy $\hbar\omega_L$, the scattered photon energies $\hbar\omega_S(2\,\mathrm{LO})$. Their intersections define the incoming ($E_0 = \hbar\omega_L$) and the outgoing resonance, $E_0 = \hbar\omega_S(\mathrm{LO})$ and $E_0 = \hbar\omega_S(2\,\mathrm{LO})$, pressures. The $\hbar\omega_S(\mathrm{LO})$ and $\hbar\omega_S(2\,\mathrm{LO})$ lines are slightly inclined to reflect the pressure shift of the phonon frequency. This shift is two orders of magnitude smaller compared to the E_0 shift.

shifts in the E_0 gap energy with pressure were determined from the observed sharp PL peaks and the data are consistent with the previous measurements (Yu and Welber 1978). The three horizontal lines drawn on the upper part of this figure represent the incident laser excitation energy $\hbar\omega_L = E_L = 1{\cdot}916\,\mathrm{eV}$ for the 647·1 nm of the krypton laser used for excitation), the LO phonon scattered energy $\hbar\omega_S(\mathrm{LO})$, and the 2 LO-phonon scattered energy $\hbar\omega_S(2\,\mathrm{LO})$, respectively. The intersections of these lines with the E_0 gap energy curve determines the RRS (to be discussed later).

3. Discussion

Resonance Raman scattering experiments in bulk GaAs near the E_0 band gap have been reported in earlier publications (Trömmer *et al* 1976; Trömmer and Cardona 1978; Yu and Welber 1978; Sood *et al* 1987). Both the LO and the 2 LO phonon enhancements have been observed and theoretically treated (Martin 1974; Zeyher

1974). However, published accounts of pressure-tuned RSS experiments on bulk GaAs have hardly touched upon the special features and the advantages of the method. For instance, it would be impossible with wavelength (incident energy) tuning to demonstrate the relationship between the PL and the 2 LO, such as the one shown in figure 4 middle frame, because of the over powering intensity of the PL. With 6471 Å radiation and pressure tuning the RRS for the 2 LO occurs at a pressure of 3·7 GPa which is close to the band crossing (direct minimum with the indirect × minima). Near band crossing the PL intensity falls off precipitously and this facilitates the observation of the PL peak and the 2 LO together which directly reveals that $\hbar\omega_S(2\,\mathrm{LO}) = E_g$.

4. The 2 LO resonance

The resonant 2 LO scattering is attributed to an iterated electron-one-phonon scattering process caused by the Frölich interaction (Martin 1974; Richter 1976; Olego and Cardona 1981), and the theoretical calculation of the Raman scattering efficiency involves perturbation theory taken to the fourth order (Richter 1976)

$$|\varepsilon_L \cdot R \cdot \varepsilon_S|^2 \propto \left| \frac{<0|\varepsilon_L \cdot P|i> \; <i|H_{\mathrm{EL}}|j> \; <j|H_{\mathrm{EL}}|k> \; <k|\varepsilon_S \cdot P|0>}{[E_i - \hbar\omega_L]\left[E_j - \hbar\omega_S \mathrm{LO} + \dfrac{\hbar^2 k^2}{2m}\right][E_k - \hbar\omega_S(2\,\mathrm{LO})]} \right|^2. \quad (1)$$

where i, j, k are the intermediate states and E_is are the corresponding energies, P the momentum operator and H_{EL} is the electron lattice interaction. In the inset to figure 4, the intermediate states involved are shown (see the conduction band). The intraband electron scattering takes place through the Frölich mechanism, and the Raman scattered intensity depends strongly on the wave vector $\boldsymbol{q}$ of the LO phonon. The three energy denominators in (1) indicate three resonances for the Raman cross section of the 2 LO phonons, at energies corresponding to $\hbar\omega_L = E_i$ (incoming) $\hbar\omega_L = E^j + \hbar\omega_{\mathrm{LO}}(q)$ (intermediate) and $\hbar\omega_{\mathrm{L}} = E_k + \hbar\omega_{2\,\mathrm{LO}}$ (outgoing channel). Since all $\boldsymbol{q}$s are allowed for second order scattering, the "intermediate" channel can be in resonance with the "incoming" or the "outgoing" channel simultaneously, leading to double resonances (Abdumalikov and Klochikhin 1977). Under special circumstances a triple resonance (Alexandrou and Cardona 1987; Alexandrou *et al* 1988) is possible, but this needs three bands, in two of which the energy separation should match the phonon energy. Resonance enhancement of 2 LO due to double resonances have been reported in GaAs, for photon energies varying across the $E_0 + \Delta_0$ gap (Olego and Cardona 1981).

5. Pressure-induced 2 LO resonance

The pressure-induced 2 LO resonance is sharply defined and narrow (see figure 2), and with 647·1 nm excitation it peaks near 3·75 GPa (see figure 2). The slight asymmetry, we believe, is due to pressure-induced transparency. For the RRS the requirement is, that an electronic energy gap in the system must become equal to the incident radiation $\hbar\omega_L$, or, to the Raman scattered radiation $\hbar\omega_S$. In the case of GaAs, the E_0

gap becomes equal to $\hbar\omega_S(2\,\text{LO})$ near 3·8 GPa for $\hbar\omega_L = 1{\cdot}916\,\text{eV}$, and this is shown by the intersection of the $\hbar\omega_S(2\,\text{LO})$ line with the E_0 vs P curve in figure 5. This is the condition for the so-called "outgoing" resonance, namely $\hbar\omega_L = E_0 + \hbar\omega_{2\,\text{LO}}$. Further when $\hbar\omega_S(2\,\text{LO}) = E_0$, the 2 LO peak should fall right on top of the PL peak, and this is beautifully borne out by the data shown in figure 4c. The inset on figure 4c schematically shows this resonant Raman process, where the conduction-valence band gap (E_0) has been precisely tuned to $E_0 \equiv \hbar\omega_S(2\,\text{LO})$. The exciting radiation $\hbar\omega_L = \hbar\omega_S + \hbar\omega_{2\,\text{LO}}$ takes an electron to the conduction band, which is scattered twice in the band (intraband Frölich mechanism) by the LO phonon, before recombining with the hole to give the Stokes radiation $\hbar\omega_S(2\,\text{LO})$. The latter exactly matches with the luminescence and, therefore, appears as a strong spike on the PL peak in figure 4c. At this point, luminescence and Raman scattering become indistinguishable. In a pressure-induced RRS experiment the "outgoing" resonance will occur first, if the energy gap increases with pressure, and this is because $\hbar\omega_S < \hbar\omega_L$.

We have also carried out RRS experiments with other excitation frequencies, viz the 568·2 nm line of the krypton laser. The energy of this line is $\hbar\omega_L = 2{\cdot}182\,\text{eV}$, and we observe a sharp pressure-induced 2 LO RRS, peaking near 6·75 GPa. From the discussion in the preceding paragraphs, this pressure should then be the point at which the E_0 gap becomes equal to $\hbar\omega_S(2\,\text{LO}) = \hbar\omega_L - \hbar\omega_{2\,\text{LO}} = 2{\cdot}10\,\text{eV}$, and this is indeed the case. Our E_0 vs P curve shown in figure 5, when extrapolated, intersects the $\hbar\omega_S(2\,\text{LO})$ line for 568·2 nm excitation precisely at this pressure, thereby showing that the scaling with $\hbar\omega_L$ is consistent. From this we conclude that the 2 LO resonance in bulk GaAs is a very sensitive and precise way to locate the E_0 gap, far beyond the Γ–X cross-over pressure. From pressure-induced RRS measurements on GaAs/AlAs thin layer superlattices, (Holtz *et al* 1989) arrive at a similar conclusion.

We believe that the pressure-induced 2 LO resonance in bulk GaAs reported in this paper is a double resonance involving the "outgoing" and "intermediate" channels. At a higher pressure a double resonance involving the "incoming" and "intermediate" channels may be expected when $E_0 + \hbar\omega_{\text{LO}} < \hbar\omega_L < E_0 + \hbar\omega_{2\,\text{LO}}$. However, we only observe the strong "outgoing" double resonance. In fact, this seems to be always the case, and has been noticed in all resonance experiments where the photon energy has been varied to bring about RRS (Zucker *et al* 1983; Sood *et al* 1985).

6. The LO resonance

The LO-resonance is shown in figure 3 and a shallow peak occurs at $\hbar\omega_L = E_0$. For the LO scattering, the Raman efficiency can be approximated by the expression (Cerdeira *et al* 1986)

$$|R|^2 \propto \left| A + \frac{B}{(\hbar\omega_L - E_0(P) + i\Gamma)(\hbar\omega_S - E_0(P) + i\Gamma)} \right|^2 \tag{2}$$

where A and B are constants, $\hbar\omega_L$ and $\hbar\omega_S$ are the energy of the incident and scattered light, $E_0(P)$ is the pressure dependent energy gap and Γ is the damping. As the gap is varied by hydrostatic pressure, the incoming resonance should occur when $E_0 = \hbar\omega_L$, and the outgoing resonance when $E_0 = \hbar\omega_S$. However, no pronounced peak is seen in the data, except the steep rise of the Raman intensity from the low pressure side. At pressures above the maximum in the LO resonance curve, the intensity decreases only by a small factor and gradually. A resonant response should exhibit symmetric shape and further the true resonance may be even smaller in magnitude when corrected for the transparency effect. Therefore, the situation is complicated by the pressure-induced transparency of the sample at pressures above 4 GPa, masking the true resonance profile.

7. Summary and conclusions

Through pressure-tuning of the E_0 gap at constant photon energy, we have observed resonance Raman scattering in bulk GaAs. A sharply defined 2 LO resonance occurs when $\hbar\omega_L = E_0 + \hbar\omega_{2\,\mathrm{LO}}$. This is the so-called "outgoing" resonance at which the E_0 gap exactly matches $\hbar\omega_S = \hbar\omega_L - \hbar\omega_{2\,\mathrm{LO}}$. For the 647·1 nm radiation ($\hbar\omega_L =$ 1·916 eV), this resonance peaks sharply at 3·75 GPa. Experiments with other incident photon energies show, that the direct gap E_0 can be precisely located using the 2 LO resonance, even at pressures far beyond the direct-indirect crossover pressures, where the PL vanishes.

We believe that the 2 LO resonance is a double resonance, mediated by the Frölich interaction, with the "intermediate" and the "outgoing" terms dominating the Raman cross section. Pressure-tuning is an attractive technique for investigating RRS and should be applicable to other group III–V and II–VI semiconductors with direct gaps. Our results on quantum well structures on GaAs substrates (Kourouklis *et al* 1990) indicate, that a strong interference from the substrates is unavoidable.

We believe that the energy vs. pressure representations similar to the one shown in figure 5 is the key diagram to understand pressure-tuned RRS.

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