Stress-Induced Doubly Resonant Raman Scattering in GaAs

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We have been able to produce conditions for doubly resonant Raman scattering where both incident and scattered light are simultaneously in resonance with an electronic interband transition, by fine tuning of the energy separation between light- and heavy-hole valence-band states using uniaxial stress. Under these conditions the Raman tensor for scattering by phonons becomes strongly asymmetric and forbidden scattering by TO phonons is also observed. The ability to approach the double resonance in a continuous manner allows direct comparison between experiment and theory and leads to a better understanding of these novel phenomena.

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Uniaxial stress splits the top of the valence band,[1] which in GaAs is doubly degenerate. By appropriate choice of stress this splitting can be made equal to one phonon energy ($\hbar\Omega_{LO}=36.7$ meV, $\hbar\Omega_{TO}=34.4$ meV). Under these conditions resonant Raman scattering experiments can be performed in which both the incoming and the scattered beams are simultaneously in resonance with electronic transitions involving the two split valence bands and the conduction band. This condition is known as doubly resonant Raman scattering (DRRS), and should be distinguished from the previously observed stress-induced single resonances.[2] We present here measurements of resonant Raman scattering in bulk GaAs under uniaxial stress in which such double resonance is unambigously observed. Under DRRS conditions, the Raman tensor for zone-center phonons is markedly asymmetric ($R_{yz} \gg R_{zy}$), and forbidden scattering by TO phonons is also observed. Such a novel type of forbidden scattering undoped semiconductors was only recently observed in short-period GaAs/AlAs superlattices.[3]

The concept of double resonance in Raman scattering by phonons has been previously discussed in the literature.[4] An early report[5] of DRRS for InSb was later proven incorrect.[6] More recently, Miller, Kleinman, and Gossard[7] observed DRRS by LO phonons in GaAs/AlAs superlattices with both incident and scattered radiation simultaneously in resonance with different fixed intersubband transitions. The method reported here enables us to fine tune in and out of the double resonance in bulk GaAs by changing the stress in a continuous manner.

Antisymmetric Raman tensors are commonly observed in scattering by electronic excitations.[8] For phonons, however, the quasistatic approximation relates the Raman tensor to derivatives of the electronic susceptibility, thus allowing only for the presence of symmetric terms in the Raman tensor.[4] Antisymmetric Raman tensors for phonons have, nevertheless, been observed in spin-disordered europium chalcogenides, as a result of magnetic interactions.[9] Here we show that, as a consequence of the DRRS condition, the quasistatic approximation breaks down and antisymmetric Raman scattering by phonons can be easily generated in bulk, nonmagnetic semiconductors. Finally, although forbidden resonant Raman scattering for LO phonons is commonplace,[4] the same effect for TO phonons has only recently been reported in short-period GaAs/AlAs superlattices.[3] Impurity scattering is known to play an important role in forbidden LO-phonon scattering.[10] Our observation of strong forbidden TO-phonon scattering under double resonance conditions can also be explained by assuming an impurity-induced wave-vector transfer. Forbidden scattering by TO phonons has already been observed in heavily doped GaAs under nonresonant conditions.[11] The double resonance allows similar observations to be made in undoped samples.

Bulk samples of GaAs were cut in parallelepipeds of $1.5\times1.5\times20$ mm^3 along the cubic axes (x, y, and z, respectively, the latter coinciding with the stress axis), and placed in a uniaxial stress apparatus[12] that allows optical measurements at $T\approx100$ K. Raman scattering experiments were performed in the $x(yz)\bar{x}$ and $x(zy)\bar{x}$ backscattering configurations with a cw LD-700 dye laser as a tunable light source. Detection of scattered light was made with conventional photon-counting electronics coupled to a Spex double monochromator. In the above configuration LO-phonon scattering is allowed (via the R_{yz} and R_{zy} components of the Raman tensor), while TO-phonon scattering is forbidden.[4] Typical spectra obtained are shown in Fig. 1, where Raman lines are seen superimposed on a luminescence background.

The presence of a uniaxial stress $X\parallel[001]$ splits the top of the valence band into two doublets of $|\frac{3}{2},\pm\frac{3}{2}\rangle$ (bottom) and $|\frac{3}{2},\pm\frac{1}{2}\rangle$ (top) symmetry.[1] The notation refers to angular momentum eigenstates where the stress direction is chosen as the quantization axis. When the laser light is close to either of the gaps between these valence bands and the bottom of the conduction band (designated by $E_g^{(3/2)}$ and $E_g^{(1/2)}$, respectively), the com-

ponents of the Raman tensor can be written as

$$R_{yz}=A+\sum_{\mathbf{k}}\frac{B}{[\hbar\omega_L-E_g^{(3/2)}(X)+i\Gamma][\hbar\omega_s-E_g^{(1/2)}(X)+i\Gamma]} \tag{1a}$$

and

$$R_{zy}=A+\sum_{\mathbf{k}}\frac{B}{[\hbar\omega_L-E_g^{(1/2)}(X)+i\Gamma][\hbar\omega_s-E_g^{(3/2)}(X)+i\Gamma]}, \tag{1b}$$

where ω_L and ω_s are the frequencies of the incident and scattered radiation, A represents the constant contribution from the nonresonant terms and B is the product of the dipole matrix elements for transitions between valence and conduction bands times the matrix elements of the electron-phonon interaction via deformation potential and electro-optical effect. The latter couples only the stress-split valence bands with each other. Lifetime broadening is represented by the phenomenological parameter Γ. The processes contributing to the Raman tensors of Eqs. (1) are sketched in Fig. 2(a). For the value of stress X_0, at which

$$E_g^{(3/2)}(X_0)-E_g^{(1/2)}(X_0)=\hbar\Omega_{\mathrm{LO}}=\hbar\omega_L-\hbar\omega_s, \tag{2}$$

both denominators in R_{yz} vanish simultaneously as $\hbar\omega_L$ approaches $E_g^{(3/2)}$ (double resonance), while R_{zy} is not resonant at this frequency. Under these conditions, the ratio of scattered intensities for both polarizations

$$\rho=(I_{yz}/I_{zy})=|R_{yz}/R_{zy}|^2 \tag{3}$$

becomes singular. This can be seen in the central part of Fig. 1(a) where the spectra for (yz), full line, and (zy), dashed line, are displayed for $X=X_0=6.0$ kbar. This figure also shows the evolution of the spectrum, for fixed stress X_0, as $\Delta\omega_L=E_g^{(3/2)}/\hbar-\omega_L$ is varied through its DRRS value [$E_g^{(3/2)}=1.547$ eV, in good agreement with the value for $E_g^{(3/2)}=1.542$ eV given in Fig. 5 of Ref. 1]. At the DRRS frequency, we observe a strong LO-phonon Raman line superimposed on a weaker broad luminescence for (yz) polarization, while for (zy) polarization only the luminescence is visible. (Note that the luminescence barely shifts with stress. This is due to the existence of a maximum in the lowest gap versus stress, see Fig. 5 of Ref. 1.) The spectrum for this polarization remains practically unaltered as ω_L changes, so we only show it for $\Delta\omega_L=0$. As the laser frequency moves away from this value, the intensity of the LO-phonon line in the (yz) spectrum decreases precipituously until it is lost in the luminescence background for $\hbar\Delta\omega_L=\pm 12$ meV. Similar results are obtained when fixing $\hbar\omega_L=1.545$ eV and varying the stress continuously in the range $0\leqq X\leqq 8$ kbar [Fig. 1(b)]. At $X_0\approx 6.0$ kbar forbidden scattering by TO phonons can also be observed in the (yz) polarization. The forbidden TO-phonon scattering is maximum at somewhat lower stress ($X_0'\approx 5.6$ kbar corresponding to $E_g^{(3/2)}-E_g^{(1/2)}=\hbar\Omega_{\mathrm{TO}}$), as can be seen in Fig. 1(c). The resonance in the TO phonon is sharper [Figs. 1(a) and 1(b)] than that for the LO phonon, the former disappearing completely when $\hbar\Delta\omega_L\approx\pm 5$ meV. Although it is not clear which mechanism induces this type of scattering, we believe that impurity-induced wave-vector transfer[11] could be responsible for this resonant behavior.

In order to compare our results with theoretical predictions we must integrate the expressions for R_{ij} of Eqs. (1) over $\mathbf{k}$ space. In performing this integration we introduce excitonic effects by use of a density of states function appropriate for a 2D M_0 singularity, which

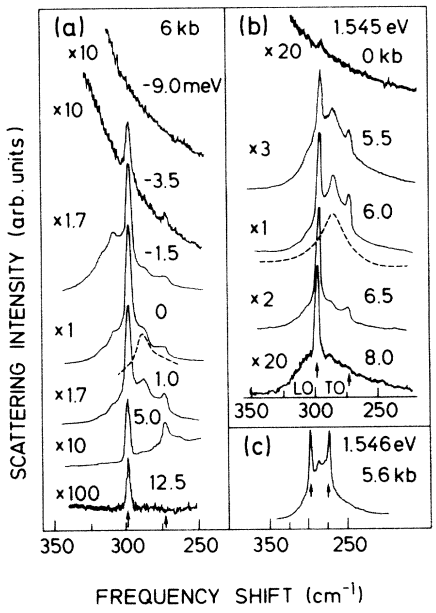

FIG. 1. Light scattering spectra of GaAs under (001) stress at $T=100$ K. Full curves show the spectra for $x(yz)\bar{x}$ configuration while the dashed curves show typical spectra for the $x(zy)\bar{x}$ configuration. In (a) we show spectra for $X=6.0$ kbar for various values of the difference between 1.547 eV and $\hbar\omega_L$. In (b) spectra for different stresses are displayed for $\hbar\omega_L=1.545$ eV. In (c) we show one spectrum where forbidden TO-phonon scattering occurs with maximum intensity. Arrows indicate the position of the LO- and TO-phonon lines. The multiplication factors next to the curves indicate that the data have been multiplied by them before plotting. Although no phonon structure is seen in the dashed line, structure nearly three orders of magnitude smaller than that in the corresponding solid lines is seen in the expanded original data. This structure, after subtraction of a smooth, Lorentzian-type luminescence background, was used in the plots of Figs. 2 and 3.

simulates the excitonic step at the band gap.[13] This procedure results in the following expressions:

$$R_{yz} = A + \frac{B/\hbar\Omega_{LO}}{x} \ln\left[\frac{(\eta - x) + i\gamma}{\eta + i\gamma}\right] \quad (4a)$$

and

$$R_{zy} = A + \frac{B/\hbar\Omega_{LO}}{2+x} \ln\left[\frac{(\eta - 1 - x) + i\gamma}{(\eta + 1) + i\gamma}\right]. \quad (4b)$$

In the above equations we use the dimensionless variables η, γ, and x defined by

$$\eta = \frac{\hbar\omega_L - E_g^{(3/2)}(X_0)}{\hbar\Omega_{LO}}, \quad \gamma = \frac{\Gamma}{\hbar\Omega_{LO}}, \quad x = \frac{X}{X_0} - 1, \quad (5)$$

The stress dependence of the gaps was approximated by

$$E_g^{(3/2)}(x) - E_g + \hbar\Omega_{LO}(1+x), \; E_g^{(1/2)}(x) - E_g, \quad (6)$$

which is reasonably obeyed in the proximity of X_0, as can be seen in Fig. 5 of Ref. 1. The ratio ρ of the Raman intensities for both polarizations is obtained by substituting Eqs. (4) into Eq. (3). The results are shown in Fig. 2(b), calculated with $\Gamma = 2.0$ meV, $E_g^{(3/2)}(X_0) = 1.547$ eV, and $X_0 = 6.0$ kbar. They are in qualitative agreement with the experiments. For $x = 0$ the ratio ρ is enhanced by almost three orders of magnitude at the double resonant peak from its value $\rho = 1.0$ far from resonance. The resonance in ρ becomes less pronounced, and more asymmetric for $x \neq 0$, i.e., when the stress-induced splitting of the valence bands is less (or more) than $\hbar\Omega_{LO}$.

Finally, in Fig. 3 we show data on the ratio ρ as a function of the stress parameter x for fixed laser frequencies. Again the resonance in ρ is more pronounced and symmetric the closer $\hbar\omega_L$ is to the double resonant condition [Eq. (2)]. Theoretical predictions based on Eqs. (3) and (4) are shown in the inset of this figure and are in general agreement with the experimental results. Although the theoretical and experimental curves for both Figs. 2 and 3 are in qualitative agreement, the former predicts a larger resonant enhancement in ρ than that observed in our experiments. This is not surprising in view of the simplicity of the model, which neglects discrete excitons and polariton effects. In Figs. 2 and 3 we can see the dramatic effect on the asymmetry of the Raman tensor as we approach the double resonance condition by fine tuning of either the stress (for fixed ω_L) or the frequency (for $X - X_0$). This tuning is more difficult in multiple quantum well structures[7] where the separation between the subbands is fixed by the growth conditions.

In summary we have observed doubly resonant Raman scattering in GaAs by continuously varying the splitting

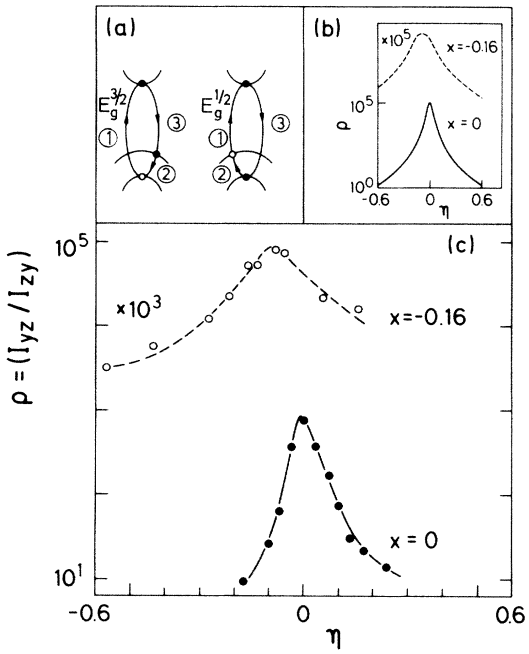

FIG. 2. (a) Raman scattering processes contributing to the double resonance. (b) Predictions of Eqs. (4) for the intensity ratio $\rho = I_{yz}/I_{zy}$ vs laser frequency, for different stresses [η and x are defined in Eq. (5)]. (c) Experimental values of ρ vs η for different stresses. Curves are only to assist the eye.

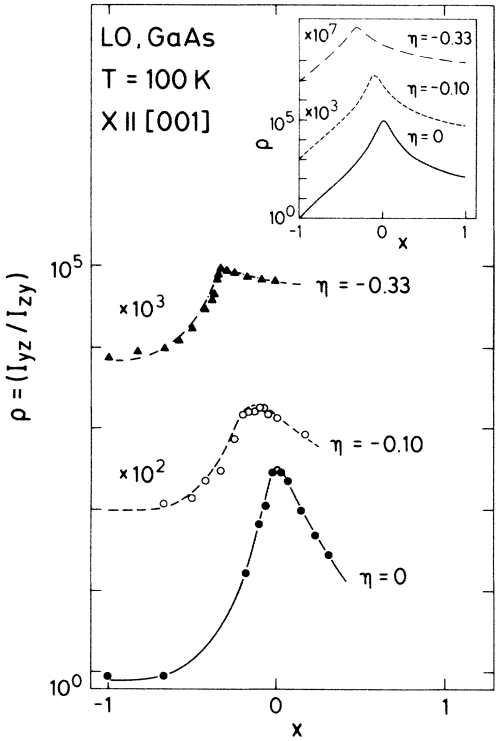

FIG. 3. Intensity ratio ρ vs stress for different laser frequencies. The inset shows the theoretical predictions of Eqs. (4).

between the light- and heavy-hole valence bands using uniaxial stress. The fine-tuning possibilities (less than 0.5 meV $< \Gamma$) of our experimental approach makes it possible to compare our results with theoretical line shapes for the resonant cross sections. We have also observed forbidden Raman scattering by TO phonons, which was only possible by tuning the double resonance within a few millielectronvolts from the DRRS condition.

We should mention that the appearance of asymmetric scattering by TO phonons has already been discussed by Zucker *et al.* for multiple quantum wells.[14]

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