

Effect of Uniaxial Stress on the Reststrahlen Spectrum of GaAs[†]

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We have measured the effect of uniaxial stress on the reststrahlen spectrum of GaAs. Measurements were performed on pure and heavily doped samples. The signs of the splittings and shifts observed for [111] and [001] stress agree with previous Raman-scattering work. We are able to obtain more complete data for the LO phonons because of differences in the Raman and infrared (ir) selection rules. The magnitudes of the shifts and splittings obtained in the ir measurements are somewhat larger than in the uniaxial Raman work. We interpret this fact as evidence for relaxation of the stress near the surface: The penetration length of the light in the Raman experiment is considerably less than in the reststrahlen region.

I. INTRODUCTION

The effect of hydrostatic pressure on the first-order Raman spectrum of semiconductors has been the object of considerable study. These measurements, which can be performed on materials either transparent¹ or opaque² to the scattered radiation, yield the mode Grüneisen parameter, γ_{Hyd} , of the optical phonons at $\vec{k}=0$. A number of studies of the effect of uniaxial stress on the Raman phonons have also been performed recently. Such studies, while limited to lower stresses because of sample fracture, yield, besides the hydrostatic Grüneisen parameter, phonon splittings produced by the pure-shear components of the stress and selection rules.³ In the materials of the Ge family the triply degenerate $\Gamma_{25'}$ phonons split into a doublet and a singlet for either [111] or [001] stress. For a [111] compression, the doublet moves to lower and the singlet to higher frequencies. The opposite occurs for [001] stress. In the zinc-blende-type semiconductors the effect just mentioned also occurs; however, it is superimposed onto the longitudinal-transverse electrostatic splitting.

Two difficulties appear in the Raman measurements under uniaxial stress. The hydrostatic Grüneisen parameters obtained from such measurements are, for opaque materials, consistently smaller than those obtained from actual hydrostatic-pressure measurements.^{2,3} As a possible source of this discrepancy a slight relaxation of the stress in the surface layer in which the scattering occurs has been suggested.^{2,3} Also, due to the selection rules and the limitations of the experimental arrangement, the behavior of the LO phonon for a [001] stress cannot be observed. In an attempt to solve these problems, we have studied the effect of uniaxial stress on the reststrahlen spectrum of GaAs, a material for which the discrepancy between hydrostatic and uniaxial Raman data is rather large.^{2,3} The reststrahlen work does not have the

selection-rules limitation mentioned above; both longitudinal and transverse phonons can be studied. The longitudinal phonons correspond to the high-energy edge and the transverse phonons to the low-energy edge of the reststrahlen band observed in the reflection spectrum. Also, the absorption length of the light in this spectral region is considerably larger than for the light of the Ar-ion laser used in the Raman work. Consequently, the effects of stress relaxation at the surface should be much smaller in the reststrahlen than in the Raman work.

The effect of uniaxial stress on the reststrahlen spectrum is best discussed in the polariton scheme. Let us consider a zinc-blende material and call \vec{W} the relative sublattice displacement which corresponds to an optical phonon. An electric field \vec{E} produces the acceleration \vec{W} and the polarization \vec{P} given by⁴

$$\vec{W} = \bar{b}^{11} \cdot \vec{W} + \bar{b}^{12} \cdot \vec{E}, \quad \vec{P} = \bar{b}^{21} \cdot \vec{W} + \bar{b}^{22} \cdot \vec{E}. \quad (1)$$

The tensors \bar{b}^{ij} have the symmetry of the crystal and thus reduce to scalars in the cubic case but not when a uniaxial stress is applied. From Eq. (1) we obtain the dielectric-constant tensor $\bar{\epsilon}$, ($\bar{\epsilon} + 4\pi\bar{P} = \bar{\epsilon} \cdot \vec{E}$):

$$\bar{\epsilon} = \bar{1} + 4\pi [\bar{b}^{22} + \bar{b}^{21}(-\omega^2 \bar{1} - \bar{b}^{11})^{-1} \bar{b}^{12}], \quad (2)$$

where $\bar{1}$ is the unit matrix. It is convenient to refer Eq. (2) to principal axes. These axes are fixed by symmetry for a stress along a high-symmetry direction ([001], [111], or [110]). Equation (2) can then be written

$$\epsilon_{jj}(\omega) = \epsilon_{jj}(\infty) + \Omega_{jj}^2 / (\omega_{\text{TO},jj}^2 - \omega^2), \quad (3)$$

where

$$\epsilon_{jj}(\infty) = 1 + 4\pi b_{jj}^{22}, \quad \Omega_{jj}^2 = 4\pi b_{jj}^{21} b_{jj}^{12}, \quad \omega_{\text{TO},jj}^2 = -b_{jj}^{11}.$$

The normal modes of vibration are found by solving Maxwell's equations with the dielectric constant of

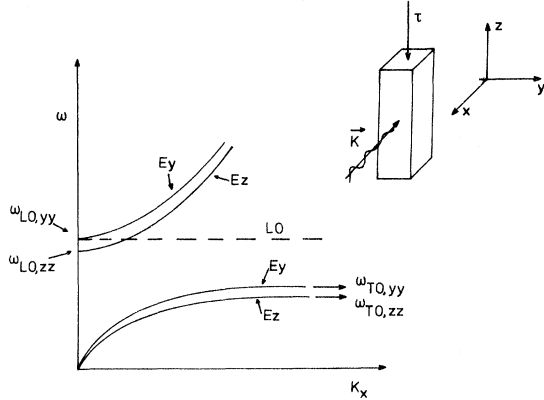


FIG. 1. Polariton dispersion relations for GaAs under a compression along [001]. The dashed line is the longitudinal vibration. The experimental configuration is also indicated.

Eq. (3). The equation $\vec{\nabla} \cdot \vec{D} = \vec{k} \cdot \vec{\epsilon} \cdot \vec{E} = 0$ has solutions for either $\epsilon = 0$ (longitudinal phonons) or for $\vec{\epsilon} \cdot \vec{E} \perp \vec{k}$ (polaritons). For a wave vector \vec{k} along a principal direction, we find from the wave equation the dispersion relation:

$$k^2 = (\omega^2/c^2) [\epsilon_{jj}(\infty) + \Omega_{jj}^2/(\omega_{TO,jj}^2 - \omega^2)]. \quad (5)$$

Equation (5) yields, for each principal direction of the vibration j , two branches of the dispersion relation $\omega(k)$. These branches, together with the longitudinal-phonon branch, are shown in Fig. 1 for a zinc-blende-type crystal compressed along the [001] direction. For this stress direction, and also for a stress along [111], symmetry requires that two principal components of the tensor $\vec{\epsilon}$, namely, those which correspond to vibrations perpendicular to the stress direction, be equal. Thus we write^{3, 5, 6}

$$\begin{aligned} \omega_{TO,\parallel}^2(\tau) &= \omega_{TO}^2 + \Delta_H(\omega_{TO}^2) + \frac{2}{3}\Delta(\omega_{TO}^2), \\ \omega_{TO,\perp}^2(\tau) &= \omega_{TO}^2 + \Delta_H(\omega_{TO}^2) - \frac{1}{3}\Delta(\omega_{TO}^2), \end{aligned} \quad (6)$$

where \parallel and \perp denote, respectively, vibrations parallel and perpendicular to the stress τ , Δ_H indicates the shift due to the hydrostatic component of the stress and Δ the splitting due to the pure-shear component. We write $\Delta(\omega_{TO}^2)$ and $\Delta_H(\omega_{TO}^2)$ in terms of the elastic compliance constants (S_{11} , S_{12} , S_{44}) and the three "independent constants" p , q , r as^{3, 5, 6}

$$\begin{aligned} \Delta_H(\omega_{TO}^2) &= \frac{1}{3}\tau(p + 2q)(S_{11} + 2S_{12}), \\ \Delta(\omega_{TO}^2) &= \begin{cases} \tau(p - q)(S_{11} - S_{12}), & \text{stress } \parallel [001] \\ \tau r S_{44}, & \text{stress } \parallel [111]. \end{cases} \end{aligned} \quad (7)$$

Similar relations are possible for the change of $\epsilon_{jj}(\infty)$ and Ω_{jj}^2 with stress. We notice in Fig. 1 that the dispersion curves for a vibration along j

have a frequency gap between $\omega_{TO,jj}$ and $\omega_{LO,jj}$ in which propagation cannot occur and the light is completely reflected. This gap corresponds to the reststrahlen band. The low-frequency threshold, or rather the inflection point of the low-frequency reststrahlen edge if broadening is included, gives the transverse frequency, $\omega_{TO,jj}$, at which the ϵ_{jj} component of the dielectric-constant tensor has a pole. The high-frequency edge gives the longitudinal frequency, $\omega_{LO,jj}$, at which ϵ_{jj} goes through zero. The effect of stress on the longitudinal frequency can be represented by expressions similar to Eqs. (6) and (7), with p , q , and r replaced by the corresponding longitudinal parameters p' , q' , and r' . These parameters can be related to the corresponding parameters of ω_{TO}^2 , Ω^2 , and $\epsilon(\infty)$ with the expression

$$\omega_{LO,jj}^2 = \omega_{TO,jj}^2 + \Omega_{jj}^2/\epsilon_{jj}(\infty). \quad (8)$$

For the III-V compounds $\Omega_{jj}^2/\epsilon_{jj}(\infty)$ is small and, as we shall see later, does not contribute within the experimental error to p' , q' , and r' .

Figure 1 indicates that it is possible to measure p , q , r and p' , q' , r' by measuring the shift in the low- and high-frequency reststrahlen edges when a [001] or a [111] stress is applied. Within the approximation made (namely, having neglected the \vec{k} dependence of the \vec{b}^{ij} tensors), these coefficients should be the same as those obtained from Raman measurements under stress.³ However, in the Raman case p' and q' cannot be obtained because of a selection rule in the required experimental configuration ($\vec{k} \perp$ stress).

II. EXPERIMENT

Our experiment consisted of measuring the infrared reflectance under uniaxial stress of both pure and highly doped GaAs in the spectral region between 32 and 40 μ . The samples were cut from single-crystal ingots supplied by Bell and Howell. They had a length of 20 mm and an equilateral triangle cross section with approximate side length 2.5 mm. The triangular cross section was chosen because it gives a wider reflecting face for a given cross-sectional area. This is advantageous in view of the low light level available in the spectral region of interest. The samples were mechanically polished and etched with a dilute solution of bromine in methanol. All samples measured had a (110) reflecting face. They were oriented with x rays so as to have their long dimension (i.e., the direction of the stress) along either [111] or [001]. A stress parallel to [111] yields the parameter r and the hydrostatic-mode Grüneisen parameter $p + 2q$. A stress parallel to [001] yields $p - q$ and also $p + 2q$, thus providing a consistency check.

A Perkin Elmer Model No. 14 double-pass monochromator with a globar as source and a Golay cell

as detector was used. The radiation was polarized either parallel or perpendicular to the stress axis with a gold-wire-grid polarizer, but it was noted that the monochromator also partially polarized the electric field in the horizontal plane (perpendicular to the stress axis). In order to measure both the light incident on and reflected by the sample a swinging aluminum mirror was introduced and removed from the light path immediately before the sample. The entire spectrometer was flushed with dry nitrogen gas so as to eliminate the absorption bands of H_2O and CO_2 . Because of the low light level, we chose to take measurements point by point at wavelengths separated by $0.1\text{-}\mu$ intervals and to integrate the noise at each wavelength for a period of 5 min.

The stress was applied to the samples with the spring-and-lever arrangement which has been extensively documented in the literature.^{7,8} Stresses up to 10^{10} dyn/cm² can be applied to undoped GaAs samples without breaking them. However, the highly doped samples withstood stresses only up to 6.5×10^9 dyn/cm² along [111], and they shattered at 2×10^9 – 3×10^9 dyn/cm² for stresses along [001].

III. RESULTS AND DISCUSSION

The reflectivity spectra of undoped and heavily doped ($N = 5 \times 10^{18}$ electrons/cm³) GaAs are shown in Fig. 2 for zero stress and for the highest [111] stress reached and with the electric field parallel to the stress direction. For the undoped sample, the high-frequency edge of the reststrahlen band is quite sharp, and hence it is possible to define the ω_{LO} frequency rather accurately as the inflection point of this edge. However, the low-frequency edge, corresponding to the ω_{TO} frequency, is much broader: This frequency and its shift with stress

can be obtained with less accuracy than ω_{LO} . In an attempt to overcome this problem, we chose to measure heavily doped samples with a plasma edge at $15\ \mu$ ($N = 5 \times 10^{18}$ electrons/cm³). Under these circumstances, the reflectivity in our spectral region is one, except in the neighborhood of the ω_{TO} frequency. At this frequency, a dip in the reflectivity is observed, corresponding to the fact that the real part of the dielectric constant becomes positive⁹ (see Fig. 2). The minimum in this dip corresponds very closely to ω_{TO} for the appropriate polarization direction. While it is easier to pinpoint the position of this minimum than the position of the corresponding edge in the undoped material, this advantage is compensated by the fact that the doped samples withstand lower stresses, especially along [001]. We nevertheless measured doped and undoped samples so as to compare stress coefficients obtained from different sources.

For undoped samples the shifts with stress of the ω_{TO} and ω_{LO} frequencies were determined by shifting the corresponding reflectivity edges so as to bring the edges as close as possible into superposition with zero-stress measurements. For doped samples, as mentioned above, the position of the reflectivity minimum was measured as a function of stress. The results obtained are shown in Fig. 3 together with least-square straight-line fits to the experimental points. The indicated error flags are the estimated accuracy with which the position of the edge or the dip in the reflectivity was measured. As mentioned earlier, the shifts due to the hydrostatic component of the stress can be obtained from either [001] or [111] measurements. We represent the corresponding mode Grüneisen parameters (logarithmic derivative of the frequency with respect to the change in volume) as $\gamma_{[001]}$ and $\gamma_{[111]}$. This parameter is related to p and q through

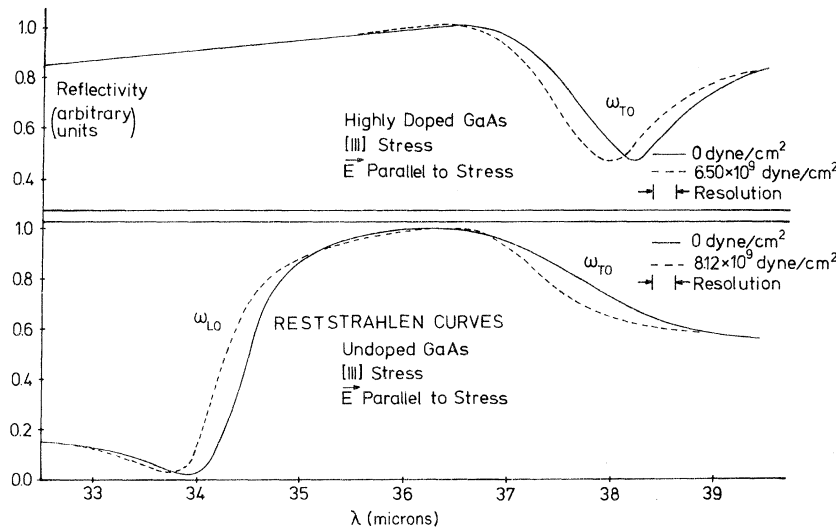


FIG. 2. Reflection spectra of an undoped and a heavily doped ($N = 5 \times 10^{18}$ electrons/cm³) GaAs sample in the reststrahlen region at room temperature for zero stress and for a high stress along [111].

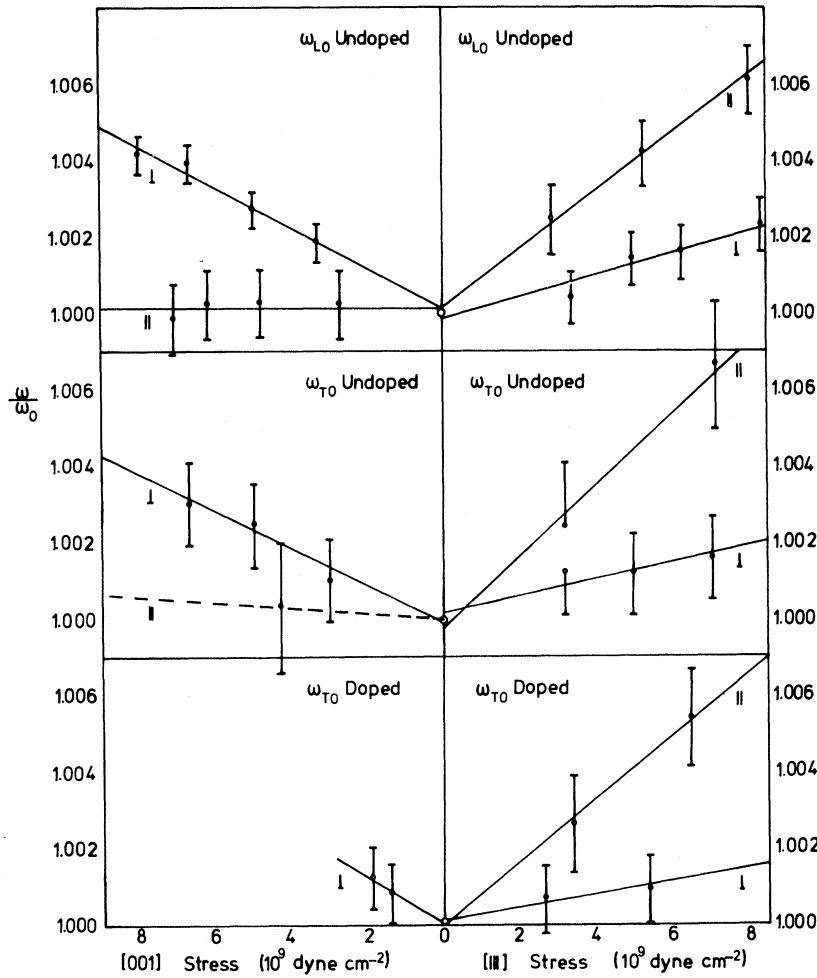


FIG. 3. Shifts of the TO and LO phonons with uniaxial stress observed for pure and heavily doped GaAs ($N = 5 \times 10^{18}$ electrons/cm³) at room temperature. Because of the low stress obtainable and very small shifts, no points were taken in the doped case for [001] stress and parallel polarization and only one point in the corresponding undoped case.

$$\gamma = (p + 2q)/6\omega_{\text{TO}}^2, \quad \gamma' = (p' + 2q')/6\omega_{\text{LO}}^2. \quad (9)$$

We list in Table I the values obtained for γ and

γ' from Fig. 3 together with the corresponding dimensionless uniaxial splitting parameters. We also list in this table the results of previous Raman

TABLE I. Results of this experiment compared with those of previous Raman work.

	ω_{LO} measurements				ω_{TO} measurements			
	From [111] $\gamma'_{[111]}$	From [001] $\gamma'_{[001]}$	From [111] $\frac{r'}{2\omega_{\text{LO}}^2}$	From [001] $\frac{p'-q'}{2\omega_{\text{LO}}^2}$	From [111] $\gamma_{[111]}$	From [001] $\gamma_{[001]}$	From [111] $\frac{r}{2\omega_{\text{TO}}^2}$	From [001] $\frac{p-q}{2\omega_{\text{TO}}^2}$
This Experiment								
Undoped	1.0 ± 0.15	0.8 ± 0.15	-0.3 ± 0.08	0.35 ± 0.08	1.0 ± 0.3	0.7 ± 0.3	-0.4 ± 0.2	0.3 ± 0.15
Doped					0.9 ± 0.25	0.9 ± 0.5	-0.4 ± 0.15	0.4 ± 0.25
Previous Raman Results								
ω_{TO} measurements								
	γ_{Hrd}^a		γ^b		$\frac{r}{2\omega_{\text{TO}}^2}^b$		$\frac{p-q}{2\omega_{\text{TO}}^2}^b$	
	1.34 ± 0.08		0.9 ± 0.3		-0.1 ± 0.1		0.1 ± 0.1	

^aFrom Ref. 2.

^bFrom Ref. 3.

measurements.^{2,3} We notice that the hydrostatic coefficients found in this work from measurements under [111] stress are marginally higher than those from [001] stress. This result, also found in the Raman work,³ suggests that in the [001] case there is a larger relaxation of the stress at the surface than in the [111] case. Our average value of γ agrees with that found in the Raman work,³ but it is definitely lower than that obtained under pure-hydrostatic pressure. Our values of $r/2\omega_{TO}^2$ and $(p-q)/2\omega_{TO}^2$ have the same sign but marginally higher magnitudes than the corresponding Raman values. Good agreement between reststrahlen work on undoped samples and that on doped samples is found.

The large experimental error margins do not allow us to ascertain any difference between p , q , r and the corresponding primed quantities. We note, however, that Raman work on II-VI compounds indicates differences between primed and unprimed coefficients well outside the experimental error.^{1,3} It would therefore be very interesting to measure the effect of uniaxial stress on the reststrahlen

spectra of these materials.

The average values of $p-q$, and r found in the present work are higher than the Raman results. We believe the reststrahlen values are more correct since the infrared absorption length¹⁰ (2200 Å at ω_{TO}) is considerably larger than that of the 4880-Å argon-laser line used in the Raman work¹¹ (900 Å): Surface-stress relaxation effects are bound to be less important the larger the absorption length. Also we note that the values of $p-q$ and r found for GaAs in Ref. 3 fall clearly below the values expected from the systematics of other III-V compounds measured.³ The present values are well in line with this systematics. We are therefore led to conclude that the measurements on GaAs reported in Ref. 3 were affected by surface relaxation of the shear stress to a greater extent than those reported here.

It is also interesting to point out that hydrostatic coefficients of electronic interband energies are lower when obtained by applying uniaxial stress than when obtained by applying pure-hydrostatic pressure.⁸

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