The restrictions ensuring constancy of the order parameter and rapid convergence limit the range of thickness in which various formulas apply from above and below, respectively. Nonlocal effects are governed by the function $f(z)$, defined in (2.20).

The generalized GL equations (2.34) and (2.39) valid close to T_c under the restrictions (2.29) and (2.30) involve the Fourier transform of the bulk weak-field kernel (2.37) evaluated at the discrete allowed wave vectors $k_j=j\pi/d$. The expressions (3.3) and (3.4) for the Fourier coefficients of the vector potential should enable one to include the effect of a net transport current. In its absence, the critical field H_c for a second-order transition is given by (2.27) or (3.11), while (3.14) gives the critical ratio below which the thermodynamic transition becomes first order.

Maki's equation (4.17) for H_c, generalized according to (4.18), is valid at all temperatures in the dirty limit ($l \ll \xi_0$) under the restrictions (4.20).

The expression (4.15), together with (4.12), valid in the range (4.21), provides the best answer for moderately impure samples at intermediate temperatures.

ACKNOWLEDGMENTS

The authors wish to thank Professor Paul Martin for numerous enlightening discussions, for his pertinent criticisms and constant encouragement. The support offered by the National Science Foundation and the Division of Engineering and Applied Physics is gratefully acknowledged. One of us (R.S.T.) would like to thank the National Science Foundation for a Predoctoral Fellowship during the initial stages of this work.

PHYSICAL REVIEW VOLUME 167, NUMBER 2 10 MARCH 1968

Raman Scattering by Coupled Optical-Phonon–Plasmon Modes in GaAs

B. TELL AND R. J. MARTIN
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 26 July 1967)

Raman scattering by coupled optical-phonon–plasmon modes has been studied in five differently doped GaAs samples in order to determine the linewidths and polarization of the coupled modes. The linewidths have been related to a lifetime which is predominantly due to individual electron collisions, although evidence is presented for Landau damping in the purest sample studied. The polarization data show that the plasma Raman scattering is comparable in magnitude to the phonon Raman scattering. The excitation wavelength was 9698 Å from the ionized xenon laser.

I. INTRODUCTION

WE have studied Raman scattering from five differently doped GaAs samples in which the conduction-electron plasma frequency varied from one-quarter to twice the longitudinal optical-phonon frequency. Mooradian and Wright[1] (called MW hereafter) have performed the only previous experiment on a coupled electron plasma-phonon system, although there have been numerous theoretical papers.[2] MW showed that the frequency and damping of the coupled modes change as a function of carrier concentration or plasma frequency. At low plasma frequencies, the modes are only weakly coupled and there exists a reasonably pure plasma line and the longitudinal (LO) and transverse (TO) optical-phonon lines. At high plasma frequencies, the modes are again uncoupled with the LO phonon approaching the TO phonon frequency. For intermediate cases, the modes have mixed phonon-plasma character with the mixing being largest where the uncoupled dispersion curves would cross.

One motivation for the present experiment was to determine the linewidths of the coupled system. The linewidths have been related to a phenomenological damping constant which is predominantly determined by collision damping. However, evidence for Landau damping in the purest sample studied is presented. The polarization of the Raman scattered light has been determined in order to discriminate among the various mechanisms which can produce phonon[3] and/or plasmon Raman scattering.[4,5] The published results of MW were obtained with unoriented samples for which

[1] A. Mooradian and G. B. Wright, Phys. Rev. Letters **16**, 999 (1966).

[2] B. Varga, Phys. Rev. **137**, A1896 (1965); K. S. Singwi and M. P. Tosi, *ibid.* **147**, 658 (1966); Y. C. Lee and N. Tzoar, *ibid.* **140**, A396 (1965); D. E. McCumber, *ibid.* **154**, 790 (1967); E. Burstein, A. Pinczuk, and S. Iwasa, *ibid.* **157**, 611 (1967); and R. Tsu and D. L. White, Ann. Phys. (N.Y.) **32**, 100 (1965).

[3] R. Loudon, Advan. Phys. **13**, 423 (1964).

[4] P. M. Platzman, Phys. Rev. **139**, A379 (1965).

[5] A. L. McWhorter, in *Proceedings of the International Conference Quantum Electronics*, edited by P. L. Kelly, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Co. Inc., New York, 1966), p. 111.

the polarization corrections are not known, so that intensity and polarization comparisons with the present results cannot be made. However, MW have recently obtained polarization data[6] with 1.065-μ excitation.

The experiment was plagued by the broadness of the plasma Raman lines. Since the integrated intensity in a Raman line is independent of the linewidth, the Raman light was therefore scattered over a wide frequency range. This complicates the determination of line centers and linewidths and obscures various effects, i.e., possible temperature dependence of the plasma frequency and Landau damping.

II. EXPERIMENTAL

The experimental setup was similar to the standard Raman arrangement. The laser was incident along a $\langle 010 \rangle$ axis and polarized along a $\langle 001 \rangle$ axis. Scattered light was collected in a small solid angle around a $\langle 100 \rangle$ axis at 90° from the incident beam and focused onto the slit of a single or double Spex 3/4 meter spectrometer. The gratings had 600 lines/mm, and were blazed at 1 μ. The slit widths commonly used gave resolution of $\approx$8 cm^{-1}. Interference filters were sometimes used.

The usual excitation was about 10 mW cw at 9698 Å from the Xe II laser. Some data were taken with approximately 3 mW cw at 8716 Å, also from the Xe II laser. The sweep time was 4 Å/min, and phase-sensitive detection with 10-sec integrating time was employed. The detector was a small cathode S-1 photomultiplier (RCA 70102B) cooled with liquid nitrogen. Phototube dark noise, scattered light, and laser instability were the limiting factors in this experiment. With the obvious exception of better signal-to-noise at the higher power levels, there was no difference in the spectra obtained when the laser intensity varied as much as 50% from the average value.

The samples were mounted on the cold finger of a vacuum Dewar. The sample temperature, with nitrogen as the refrigerant, was measured to be approximately 90°K. By increasing the thermal impedance to the cold finger, an intermediate temperature of around 135°K was maintained, which proved to be convenient for most purposes.

Data were obtained on all samples with 9698 Å excitation. Data were also obtained on the two least heavily doped samples with 8716 Å, but the more heavily doped samples exhibited strong fluorescence. The samples were approximately 0.5 cm on all dimensions and were oriented along $\langle 100 \rangle$ axes. The incident and scattered light propagated along cubic axes. The incident light was polarized normal to the scattering plane and therefore parallel to the third cubic axis.

The baselines chosen for the frequency and linewidth measurements were determined from a knowledge of the scattered light or laser tail and of the background level. The background level was taken at a flat portion of the spectra in the vicinity of the line of interest. The tail was determined by obtaining a Raman spectra with the beam within the sample, and then moving the sample slightly so that the beam skimmed the front of the sample. In the latter case, the scattered light completely obscured the Raman signal, so that the profile of the scattered light could be obtained. This profile did not vary significantly from what one could draw in freehand. The scattered light profiles determined were not always identical, even for a given sample at a specific temperature. Possible explanations for these differences are slightly different focusing of the incident and/or scattered light, different sections of the crystal which may scatter different amounts, and slightly different positioning of an interference filter. A discussion of the errors involved in the case where choice of the baselines is critical to our results is given below.

The crystals were purchased from the Monsanto Co. and chosen for the highest mobility consistent with the best homogeneity. The resistivity and Hall mobility were measured for all samples at room and N_2 temperature from an adjacent slice, or from a slice of the sample used for the Raman scattering, by the Van de Pauw technique.[7] The carrier concentration was calculated by assuming that the Hall mobility was equal to the conductivity mobility. The conductivity of the purest sample studied was measured at several temperatures between room temperature and nitrogen temperature, and exhibited a broad peak near 150°K. The peak conductivity value was about 10% larger than at room temperature. By interpolating the measured carrier concentrations at room temperature and nitrogen temperature to the intermediate temperatures, the mobility at these temperatures was determined. For the more heavily doped samples, the mobility at intermediate temperatures was assumed to be the same as at nitrogen temperature. The complete results are given in Table I. The room-temperature measurements are in fair agreement with the supplier's values.

TABLE I. Mobility, carrier concentration.

Monsanto catalog No.	Temp.	μ_H(cm^2/V sec)	τ_c(10^{-14} sec)	n(No./cm^3)
G1122	Room	4500	17.7	5.1×10^{16}
	135°K	5600	22.0	4.5×10^{16}
	77°K	5000	19.6	4.2×10^{16}
G346	Room	4000	15.8	1.6×10^{17}
	77°K	4100	16.1	1.4×10^{17}
C4–180	Room	3500	13.8	2.6×10^{17}
	77°K	3200	12.6	2.5×10^{17}
C2–466	Room	2900	11.4	8.6×10^{17}
	77°K	2800	11.0	8.6×10^{17}
C2–366	Room	2000	7.9	3.1×10^{18}
	77°K	2200	8.7	3.2×10^{18}

[6] A. Mooradian, Bull. Am. Phys. Soc. **12**, 340 (1967).

[7] L. J. Van de Pauw, Philips Res. Repts. **13**, 1 (1958).

III. THEORY AND DISCUSSION

We will consider the plasma-phonon system by the dielectric-constant method, employed by Varga[2] and Singwi and Tosi.[2] We follow the latter authors in that we ascribe a phenomenological damping constant to the plasma modes and neglect phonon damping which, in GaAs, is an order of magnitude smaller.

The dielectric constant in the zero-wavelength limit for the combined system is given by

$$\epsilon_T=(\epsilon_0\omega_0^2-\epsilon_\infty\omega^2)/(\omega_0^2-\omega^2)-\omega_p^2/\omega(\omega+i/\tau), \quad (1)$$

where ϵ_0, ϵ_∞ are the static and high-frequency dielectric constants, $\omega_0/2\pi$ is the transverse optical-phonon frequency, $\omega_p/2\pi=(1/2\pi)(4\pi ne^2/m^*)^{1/2}$ is the plasma frequency, and τ is a phenomenological lifetime.

The longitudinal solutions are the roots of the equation when the total dielectric constant is zero. In the absence of damping, the solutions are readily soluble and yield the coupled phonon-plasma dispersion curve. The dispersion curve along with the experimental points is presented in Fig. 1, and is similar to that previously presented by MW. In Fig. 2, the Raman spectra of several samples are presented.

With damping, solutions were obtained numerically for various values of ω_p and τ. The values of τ chosen lie between 3.9×10^{-14} to 19.6×10^{-14} sec and correspond to electron mobilities of 1000 to 5000 cm^2/V sec, respectively, encompassing the range obtained in the present experiment. The results of a computer calculation for the imaginary parts of the coupled modes for the several plasma frequencies studied in the present experiment are given in Fig. 3. The real part is slightly shifted to lower frequency for short τ, but approaches the collisionless value for the experimental τ. Varga[2] has introduced phonon strength and Burstein *et al.*[2] the plasmon strength to denote the distribution of energy which is phononlike or plasmonlike.

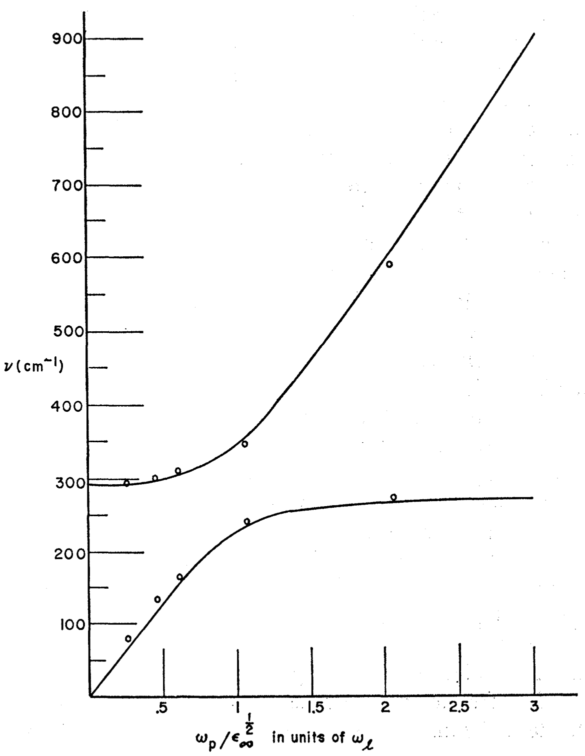

FIG. 1. The coupled LO phonon-plasmon dispersion curve along with the experimental points, calculated from Eq. (1) for $\omega_0/2\pi=269$ cm^{-1}, $\omega_l/2\pi=(\epsilon_0/\epsilon_\infty)^{1/2}\omega_0/2\pi=293$ cm^{-1}, $m^*=0.07m$.

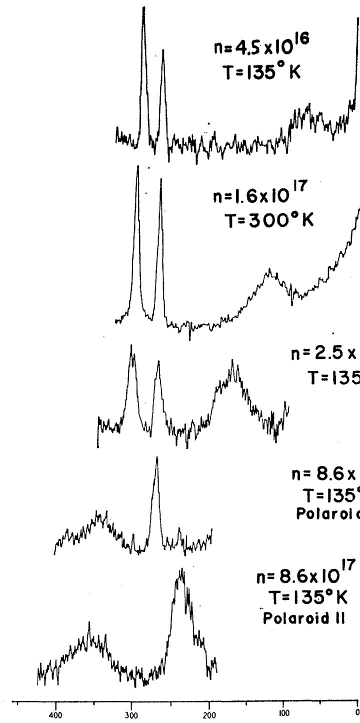

FIG. 2. Recorder traces of the Stokes-Raman spectra of several differently doped GaAs samples obtained with 9698-Å excitation.

From Fig. 3, it is seen that the damping of the modes depends strongly on the distance from the uncoupled crossover point. Below the crossover point, most of the plasma strength and consequently the damping is in the low-frequency mode (L), and above the crossover point the plasma strength and damping is mostly in the high-frequency mode (H).

The frequency and linewidth of the coupled modes were determined by hand-smoothing the experimental spectra and comparing with an assumed Lorentzian shape after subtracting out the laser tail, correcting for filters when used, and averaging the noise. The results were compared to a formula of the type

$$I(\nu)\sim\nu_p''/[(\nu-\nu_p')^2+\nu_p''^2], \quad (2)$$

where ν_p' and ν_p'' are the real and imaginary parts of a mixed mode (the frequency and the half-width at half-maximum in cm^{-1}). The experimental results are given in Table II and compared with the calculated values. The agreement between the experimental and calcu-

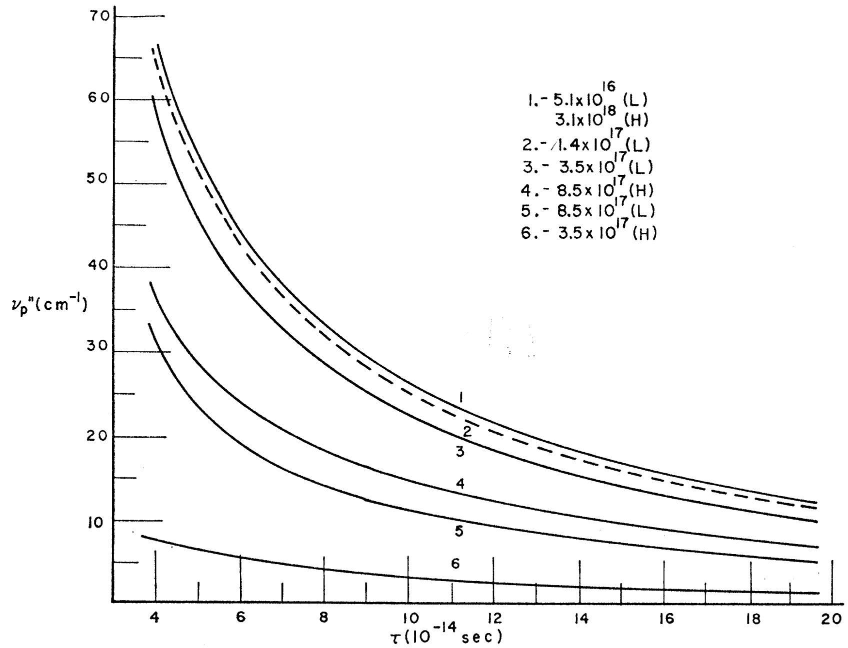

FIG. 3. The results of a computer calculation for the imaginary part of the plasma frequency. Two of the carrier concentrations differ somewhat from the final measured value. The postscripts H and L refer to the high- and low-frequency coupled modes.

lated results is reasonable, for data obtained from the three purer samples. The more heavily doped samples are considerably broader than expected. The most probable cause of this discrepancy is concentration inhomogeneities. Although the extreme breadth of the high-plasma strength lines and the background makes accurate measurement difficult, the data presented is an average of several runs for which the linewidths were reproducible to within 10 to 15% and the frequencies to several wave numbers.

It is evident from the spectra that the integrated intensity of the plasma Raman scattering is comparable to or greater than the phonon Raman lines. A spectrum taken at 8716 Å on the purest sample indicates a further enhancement of the plasma line relative to the phonon lines. For Raman scattering by individual electrons[8] and by collective waves,[9,10] a resonant enhancement factor of $[E_G^2/(E_G^2-(\hbar\omega_i)^2)]^2$ enters into the cross section. (E_G is the band-gap energy, which is $\sim$8700 Å at room temperature, and $\hbar\omega_i$ is the incident photon energy.) However, under the conditions of the present experiment, absolute cross sections are extremely difficult to measure. Even relative cross sections, with respect to the phonons, would have to be corrected for absorption which varies rapidly with temperature and wavelength for the heavier doped samples, particularly near 8716 Å. However, relative cross sections might not be particularly enlightening since the phonon enhancement factors are not known.

Finally, our data cannot be directly compared with the published data of MW since their results were obtained with unoriented samples for which the polarization corrections are not known. Consequently, no definitive results have been obtained concerning the resonant enhancement factors.

The polarization data for these samples are also of interest. In the zinc blende-type crystals (T_d symmetry) the phonon Raman scattered light is depolarized for the incident and scattered light propagating at 90° to each other and along cubic or ⟨100⟩ axes,[3] while Raman scattering from individual electrons[8] and plasmons[5] had been expected to have the same polarization as the incident light. However, recent theories due to Burstein *et al.*,[2] and to McWhorter and Argyres[9] suggest that there should also be a depolarized component, which is attributed to the phonon strength and to the total macroscopic electric field associated with the phonon-plasmon system. Furthermore, Burstein *et al.* predict that the depolarized component will predominate in zinc blende-type crystals.

The Raman scattered light in the low-frequency line in all samples (the polarization in the highest density sample was not checked) was polarized parallel to the incident polarization (by at least a factor of 5), while the high-frequency mode in the three lowest carrier concentration samples and the TO mode were in all instances depolarized. For a sample in the crossover region ($n \simeq 8.6\times10^{17}$ cm^{-3}), the high-frequency line had comparable polarized and depolarized components while the low-frequency line was polarized parallel to the incident beam (at 9698 Å excitation and 135°K). We have attempted to obtain a spectrum of this sample with 8716-Å excitation, but fluorescence from the sample obscured any possible Raman signals.

[8] P. A. Wolff, Phys. Rev. Letters **16**, 225 (1966).
[9] A. L. McWhorter and P. N. Argyres, Bull. Am. Phys. Soc. **12**, 102 (1967).
[10] P. M. Platzman, private communication and to be published.

TABLE II. Observed and calculated frequency and half-width at half-maximum.

Sample No.	Temperature (°K)	Calculated frequency and half-width (cm^{-1})		Observed frequency and half-width (cm^{-1})	
G1122[a]	300	103	33	80	35
	135	85	20	83	25
	90	80	18	80	18
G–346	135	125	16	136	20
C4–180	135	155	21	165	23
C2–466	135	355	13	347	20
		235	10	237	13
C2–366	135	615	31	590	38

[a] The calculated frequency and half-width for this sample includes corrections as discussed in the text.

The recorder traces and hand-smoothed curves compared with Lorentzian line shapes are given in Figs. 4a and 4b, for sample G1122 at three temperatures. In this figure, the choice of baseline, although somewhat ambiguous, was determined from a knowledge of the laser tail and from the background level. If the baselines were shifted by 10% of the peak height, the linewidth would also shift by around 10%. Shifts of magnitude greater than 10 to 20% yield baselines which appear to us to be unreasonable. Furthermore, several runs were taken at each temperature with a resulting consistency of better than 15% in linewidth and 5 cm^{-1} in frequency. We therefore judge that the errors in the linewidths are no worse than 20%. The baselines are not necessarily identical for the three temperatures because of variations in scattered light and signal strength as previously discussed.

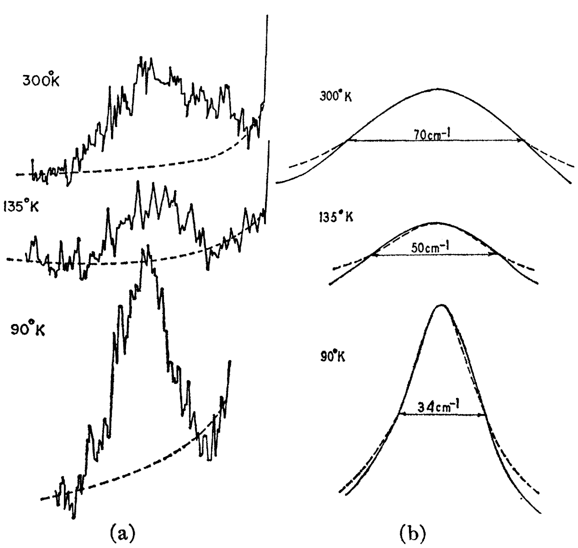

FIG. 4. (a) Recorder traces of the Raman spectra of sample G1122 at three temperatures, and (b) hand-smoothed curves (solid lines) compared to a Lorentzian shape (dashed lines), including a small correction for a filter.

We believe that effects of Landau damping have been observed. Such damping becomes significant if the average individual electron velocity is only slightly less than the plasma phase velocity (or equivalently the Debye length is comparable to a wavelength), since more electrons would extract energy from the collective oscillation than would yield energy, resulting in a damping or energy extraction from the wave. Landau damping could be observed as a function of temperature since the thermal velocity and the Debye length decrease with decreasing temperature. Sample G1122 represents the most favorable case in the present circumstances since the collision broadening is the smallest and the plasma phase velocity the slowest of the samples studied. For this sample, a significant reduction in linewidth has been observed as a function of temperature, which should be independent of concentration inhomogeneities. The more heavily doped samples, which have lower mobility and shorter Debye length, did not exhibit an appreciable temperature-dependent linewidth change.

Sample G1122 is nondegenerate until below nitrogen temperature, and is only weakly coupled to the LO phonon, so that the dispersion relation will be taken for an uncoupled nondegenerate plasma. Neglecting damping, the dispersion relation for finite wave vector k is given by[11,12]

$$\omega^2=\omega_p^2/\epsilon_0+3k^2v^2=\omega_p^2/\epsilon_0[1+3k^2\lambda_D^2], \quad (3)$$

where $v^2=KT/m$ is the one-dimensional rms thermal velocity and $\lambda_D=(KT\epsilon_0/4\pi ne^2)^{1/2}$ is the Debye length.

The Debye length λ_D varies from 1.9×10^{-6} cm at room temperature to 1.2×10^{-6} cm at 90°K. The wave vector k for right-angle Raman scattering with 9698 Å excitation is 3.2×10^5 cm^{-1}, so that the product $k\lambda_D$ varies from 0.61 at room temperature to 0.38 at 90°K. According to Jackson,[11] the simple dispersion relation

[11] J. D. Jackson, J. Nucl. Energy: Pt. C **1**, 171 (1960).
[12] P. M. Platzman and S. J. Buchsbaum, Phys. Fluids **4**, 1288 (1961).

TABLE III. Observed and calculated half-width for sample G1122.

Temperature	λ_D(cm)	$1/2\tau_c$ (cm^{-1})	$1/\tau_L$ (cm^{-1})	$1/\tau$ (cm^{-1})	Experimental (cm^{-1})
Room	1.9×10^{-6}	15	18	33	35 ± 6
135°K	1.4×10^{-6}	12	8	20	25 ± 5
90°K	1.2×10^{-6}	14	4	18	18 ± 3

given above is adequate until the product $k\lambda_D$ is slightly greater than unity. From this relation, we would expect a frequency of 103 cm^{-1} at room temperature and 80 cm^{-1} at 90°K. In both cases, the observed frequency was 80 cm^{-1}, so that the room-temperature discrepancy is outside of our experimental error.

The above dispersion relationship is obtained by assuming that collisions are rare, which, however, is not the situation in GaAs. According to Van Kampen,[13] when collisions are frequent enough to ensure that a local Maxwellian distribution is maintained, the applicable dispersion relation is

$$\omega^2=\omega_p^2+(5/3)k^2v^2. \tag{4}$$

This formula agrees better with the experimental results, yielding frequencies of 89 and 76 cm^{-1} at room temperature and 90°K, respectively. The former discrepancy still lies outside the limits of our experimental error.

The half-width of a plasma line is given by

$$2\pi\nu_p''=1/2\tau_c+1/\tau_L, \tag{5}$$

where τ_c is the electron collision time determined from the measured mobility and τ_L is the Landau damping time given by

$$1/\tau_L\simeq(\tfrac{1}{8}\pi)^{1/2}\omega_p(\omega_p/kv)^3\exp(-\omega^2/2k^2v^2). \tag{6}$$

This formula for Landau damping can be obtained[11,12] from a Boltzmann equation when the approximation $kv\ll\omega$ is used in solving for the real part (the dispersion relation) and the imaginary part (the damping) of the dispersion integral. The approximate formula for the real part agrees with numerical evaluation of the dispersion integral until $k\lambda_D>1$ as mentioned above, while the approximate result for the imaginary part deviates for $k\lambda_D>0.3$. The resulting values for τ_L are therefore taken from the numerical solutions of Jackson.[11] The results are that $1/\tau_L$ varies from approximately 18 cm^{-1} at room temperature to approximately 4 cm^{-1} at 90°K. The values for the half-widths in terms of the collision damping and Landau damping are given in Table III, and agree surprisingly well with the experimental width. As previously mentioned, G1122 was the only sample in which a significant reduction in linewidth was observed as a function of temperature. For example, the calculated contribution of Landau damping to the half-width at room temperature for sample G346 was only about 4 cm^{-1}, and for the heavier doped samples the calculated contribution is further reduced.

In conclusion, we feel that although agreement between calculated and observed values could be improved, such agreement will probably await the availability of more homogeneous and higher-mobility samples. We believe that the presence of Landau damping has been observed, even though the accompanying frequency shifts have not been seen. Furthermore, we feel that the polarization data show that the plasma Raman scattering is comparable to the phonon Raman scattering in GaAs.

Note added in proof. The polarization data of Mooradian and McWhorter has recently been published [Phys. Rev. Letters **19**, 849 (1967)]. In their notation, our polarization measurements were $(\perp, \|)$ and $(\perp, \perp)$ corresponding to, in our notation, crossed polarization and parallel polarization, respectively. We have not measured the $(\|, \|)$ or the $(\|, \perp)$ configuration. The confusing correspondence results from their designation of the scattering plane as the reference, while we have designated the incident laser polarization as the reference.

They predict, and have observed, an anomaly, i.e., a zero or near zero, in the $(\perp, \|)$ scattering cross section at carrier concentrations near 4×10^{17} cm^{-3} for the low-frequency mode. In our case, the low-frequency mode is simply not observed at any concentration for the $(\perp, \|)$ configuration, but appears only for the $(\perp, \perp)$ configuration.

ACKNOWLEDGMENTS

We wish to thank D. J. Brangaccio and D. MacNair for assistance with laser and cathode design and construction. We acknowledge several informative discussions with P. M. Platzman, and we thank S. J. Buchsbaum for comments on the manuscript.

[13] N. G. Van Kampen, Physica **21**, 949 (1955).