Longitudinal-Optical-Phonon–Plasmon Coupling in GaAs†

C. G. Olson and D. W. Lynch
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010
(Received 12 August 1968)

Infrared reflectivity measurements have been made at 78°K on three samples of GaAs, doped with Te so that the plasma frequency is nearly equal to the long-wavelength LO phonon frequency. There are two prominent dips in the reflectivity spectra, but instead of occurring near the plasma frequency and LO mode frequency, they occur at the frequencies of the two normal modes of the coupled plasmon–LO-phonon system, as predicted by Varga and by Singwi and Tosi. From the reflectivity spectra at 78°K, values of the electron effective mass of 0.067, 0.073, and $0.077m_e$ are obtained for n-type GaAs with 7.22×10^{17}, 8.75×10^{17}, and 14.0×10^{17} carriers per cm^3.

INTRODUCTION

THE coupling between plasmons and LO phonons in polar crystals has been discussed recently by Varga[1] and by Singwi and Tosi.[2] Since the long-wavelength LO lattice vibrational modes give rise to electric dipole moments which can couple to the electric field of the plasmons, longitudinal collective excitations of the electron gas, these two types of excitations are replaced by new excitations having different frequencies and mixed phonon-plasmon character. The effects of the coupling are especially marked when the long-wavelength LO mode frequency ω_1 is approximately equal to the plasma frequency ω_p, where

$$\omega_p=(4\pi Ne^2/m^*\epsilon_\infty)^{1/2}. \quad (1)$$

Here N is the electron concentration, m^* is the electron effective mass, and ϵ_∞ is the optical dielectric constant. These modes have subsequently been observed in GaAs by Raman scattering[3–5] and the frequency shift of a "phonon" was observed earlier in PbTe by inelastic neutron scattering.[6]

Although these longitudinal modes do not interact with radiation incident normally on a solid, they do influence the normal reflectivity, for they determine the zeroes of the frequency-dependent dielectric constant, or alternatively, their frequencies are given by such zeroes.[1] Singwi and Tosi[2] calculated the normal reflectivity for a typical III-V semiconductor, GaSb, and showed that the reflectivity spectrum would exhibit characteristic structure at the coupled-mode frequencies provided there was not too much damping in the electron gas. They used undamped phonons, but presumably too much phonon damping would also obscure the characteristic structure. The principal assumption in the theory is that the electrons and lattice contribute additively to the dielectric response function.

In the present paper we report the normal-incidence reflectivity at 78°K of several GaAs samples doped so that $\omega_1\approx\omega_p$. These reflectivity curves can be fitted very well by using one oscillator for the phonons and one (zero frequency) oscillator for the electrons. The features of the spectrum described by the theory are present. Since this work was begun, two reports of similar measurements have appeared, a paper[7] on GaP, and an analysis[8] of data on CdS, for which, however, no plasmon-damping information is available. The reflectivity of doped GaP does not show the characteristic "two-dip" structure predicted, because there is too much plasmon damping.

EXPERIMENTAL

The samples were purchased from Monsanto. In all cases they were tellurium-doped, boat-grown single crystals. One portion of each slice was ground flat and polished with alumina. Just before use, the sample was etched in a solution of H_2SO_4, H_2O_2, and H_2O in proportions 6:1:3. A square rod was cut from adjoining material and used for room and liquid-nitrogen temperature Hall-coefficient and resistivity measurements.

A Perkin-Elmer model 99 monochromator was used. The sample and a reference mirror were clamped into a sample holder on the tail of a liquid-nitrogen cryostat with a CsI window. The beam from the monochromator was refocused by a spherical mirror on the sample at an average angle of incidence of 8°. The reflected beam was intercepted by a flat mirror or reststrahl plate and directed to a thermocouple. LiF, NaF, CaF_2, and NaCl reststrahl plates were used over the range where they reflected more than 60% of the desired wavelength. In addition, when the CsI prism was used at wavelengths below 40 μm, a Perkin-Elmer transmission filter (range: 25–40 μm) was used immediately behind the exit slit. With this filtering, the short-wavelength stray light was less than 1%. Because of the geometry, light reflected from the front surface of the cryostat window did not

† Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2387.
[1] B. B. Varga, Phys. Rev. **137**, A1896 (1965).
[2] K. S. Singwi and M. P. Tosi, Phys. Rev. **147**, 658 (1966).
[3] A. Mooradian and G. B. Wright, Phys. Rev. Letters **16**, 999 (1966).
[4] A. Mooradian and A. L. McWhorter, Phys. Rev. Letters **19**, 849 (1967).
[5] B. Tell and R. J. Martin, Phys. Rev. **167**, 381 (1968).
[6] R. A. Cowley and G. Dolling, Phys. Rev. Letters **14**, 549 (1965).
[7] M. Hashimoto and I. Akasaki, Phys. Letters **25A**, 38 (1967).
[8] R. J. Bell, T. J. McMahon, and D. G. Rathbun, J. Appl. Phys. **39**, 48 (1968).

hit the intercept mirror. Back-surface-window reflections, diffuse scattering, and sample-holder reflections had a path length significantly different from that of the main beam. The thermocouple focusing system is very path-length-dependent, and the stray signal is effectively rejected. Tests with the sample holder empty show that this type of stray light is less than 0.1% of the detected signal.

The reference was a fresh aluminum mirror with a reflectivity of 98.4%. This was determined both by comparison to a fresh silver mirror and by a room-temperature absolute reflectance measurement.[9]

Resistivity ρ, and Hall-coefficient R, measurements were made at two places on each sample. Samples 2 and 3 were slightly inhomogeneous with a 6% difference in Hall coefficients at the two places. In all three samples the Hall coefficients were the same at 78 and 300°K. There is some uncertainty in relating the Hall coefficient to the carrier concentration via the equation $R=-A/Ne$. If the relaxation time approximation is valid and the samples are highly degenerate, then $A=1.0$. This is frequently used, but the samples used here are not yet in this limit. If all scattering at 78°K is by ionized impurities,[10] and if the carriers are in a parabolic band with $m^*=0.070m_e$, then for our samples $A=1.08$. This is the value that we used. At room temperature there may be some optical-mode scattering[11] which would change the value of A. For our samples the value of R was the same at 78 and at 300°K. We believe that N is the same at both temperatures. (This is supported by the observation that the reflection spectra of our samples were the same at 78 and at 300°K, while a 2% change in N should produce a noticeable difference.) The degree of degeneracy is lower at 300 than at 78°K, so A should increase. That it does not seem to do so may be a manifestation of some optical-mode scattering.

There is also an uncertainty in the effective mass. Spitzer and Whelan[12] have determined the effective mass for samples in this concentration range from reflectivity measurements, which give N/m^*, and transport measurements, which give N. They report a room-temperature value of $0.079m_e$ for samples of our concentration, assuming a value of 1.0 for A. Faraday rotation measurements by DeMeis and Paul,[13] using a wedge-shaped sample to avoid multiple reflections, gave values for N/m^{*2}. Their value of m^* for samples in our concentration range is $0.070m_e$ at room temperature, using $A=1$. This is still, however, dependent upon a transport-measured N.

[9] P. L. Hartman and E. Logothetis, Appl. Opt. **3**, 255 (1964).
[10] O V. Emel'yanenko and D. N. Nasledov, Fiz. Tverd. Tela **1**, 985 (1959) [English transl.: Soviet Phys.—Solid State **1**, 906 (1959)].
[11] H. Ehrenreich, Phys. Rev. **120**, 1951 (1960).
[12] W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959).
[13] W. M. DeMeis and W. Paul (unpublished); also, Harvard University Technical Report No. HP-15, 1965 (unpublished).

RESULTS

Figures 1–3 show the measured reflectivities of our samples at 78°K and calculated values using a two-oscillator fit for the normal incidence reflectivity,

$$\mathcal{R}=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \tag{2}$$

with

$$n^2-k^2=\epsilon_1, \quad 2nk=\epsilon_2. \tag{3}$$

(In the figures we have plotted the more conventional spectroscopic abcissa, wave number $\bar{\nu}=\omega/2\pi c$.) The real and imaginary parts of the dielectric constant are

$$\epsilon_1=\epsilon_\infty+\frac{4\pi\rho[1-(\omega/\omega_t)^2]}{[1-(\omega/\omega_t)^2]^2+(\omega\gamma/\omega_t^2)^2}-\frac{\omega_p^2\epsilon_\infty\tau^2}{1+\omega^2\tau^2} \tag{4}$$

and

$$\epsilon_2=\frac{4\pi\rho(\omega\gamma/\omega_t^2)}{[1-(\omega/\omega_t)^2]^2+(\omega\gamma/\omega_t^2)^2}+\frac{\omega_p^2\epsilon_\infty\tau}{\omega(1+\omega^2\tau^2)}. \tag{5}$$

Here $4\pi\rho=\epsilon_0-\epsilon_\infty$, the difference between the static and optical dielectric constants. ω_t is the frequency of the long-wavelength TO modes of the lattice and is related to ω_1 by the Lyddane-Sachs-Teller relation,[14,15] $\omega_1/\omega_t=(\epsilon_0/\epsilon_\infty)^{1/2}$. The value of ω_t, 51.52×10^{12} sec^{-1}, was chosen to agree with that found by Hass and Henvis[16] for purer GaAs at 4.2°K. ϵ_∞ was set equal to 11.2, a value obtained from refractive index measurements.[17] The lattice mode strength $4\pi\rho$, the lattice damping γ, the plasma frequency ω_p, and the plasmon lifetime τ, were varied to get the best fit to the measured reflection

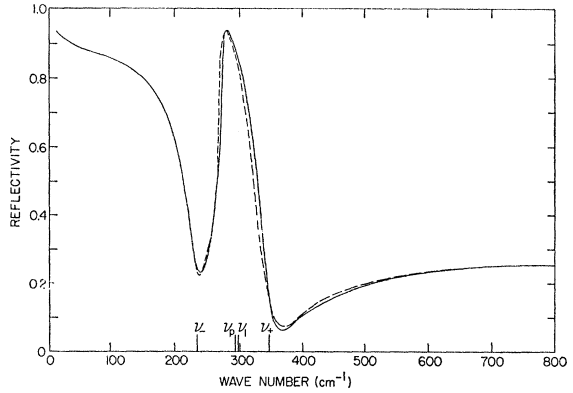

FIG. 1. Reflectivity of GaAs sample 1. Solid line, two oscillator fit as described in the text; dashed line, experimental data. Where the dashed line is not shown, it coincides with solid line, except below 210 cm^{-1}, where data were not taken. The spectral band pass was small on the scale to which the data are plotted, typical values being 4.5 cm^{-1} at 225 cm^{-1} and 3 cm^{-1} at 350 cm^{-1}. The positions of the uncoupled LO and plasmon modes as well as the two coupled modes are shown along the abcissa scale.

[14] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).
[15] W. Cochran, Z. Krist. **112**, 465 (1959).
[16] M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).
[17] D. T. F. Marple, J. Appl. Phys. **35**, 1241 (1964).

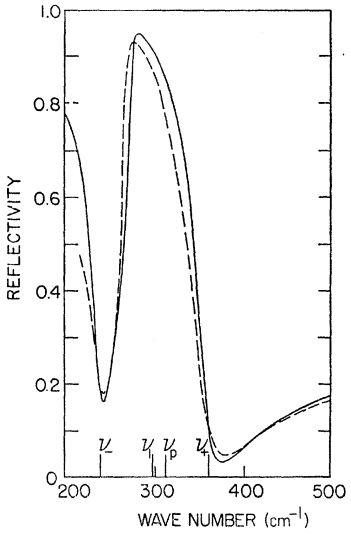

FIG. 2. Reflectivity of GaAs sample 2. See caption of Fig. 1.

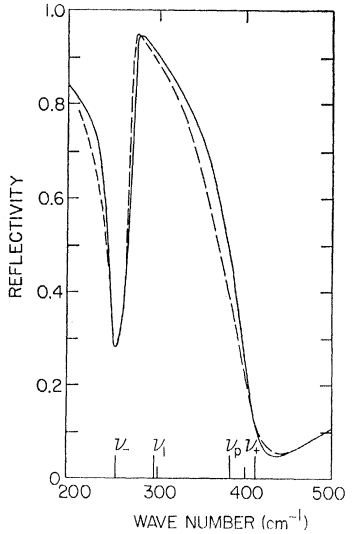

FIG. 3. Reflectivity of GaAs sample 3. See caption of Fig. 1.

spectra for which the two varied phonon parameters were the same for each sample. The primary criterion in determining the best fit was the frequency of the maximum and the two minima. The strength arrived at, 2.0, was the same as found by Hass and Henvis,[16] and our value of γ, 0.40, agrees with theirs within the uncertainty of the fit. The fit was not sensitive to changes of less than 10% in the damping. It was, however, very sensitive to plasma frequency. Changes of 1% would move the high-frequency minimum significant amounts.

The two sharp dips in the reflectivity spectrum, as ω increases, usually occur near ω_1 and ω_p, while the sharp rise as ω increases occurs near ω_t. In two of our samples, there is almost maximum coupling between the LO phonons and the plasmons, and we expect the features at ω_p and ω_1 to occur at ω_+ and ω_- or at ω_- and ω_+ (depending on whether or not $\omega_p > \omega_1$), where ω_+ and ω_- are solutions of[2]

$$2\omega_\pm^2 = (\omega_1^2+\omega_p^2) \pm [(\omega_1^2-\omega_p^2)^2+16C^2\omega_1\omega_p]^{1/2}, \quad (6)$$

with the coupling constant C given by

$$C = \tfrac{1}{2}[\omega_1\omega_p(1-\epsilon_\infty/\epsilon_0)]^{1/2}. \quad (7)$$

Equation (6) is valid only in the limit of no damping. As the damping coefficients increase, the frequencies $\omega_\pm$ will shift, becoming complex. Their real parts will be less different than Eq. (6) implies, and the steep dips in the reflectivity will become less steep, finally disappearing for large damping.[2] (For the doped GaP sample whose reflectivity is reported in Ref. 7, $\tau = 0.004\times10^{-12}$ sec, much smaller than that for our GaAs samples. This increased damping accounts for the occurrence of only one dip in the reflectivity of GaP.) We have solved Eq. (6) for our samples and have marked ω_1, ω_p, ω_+, and ω_- in Figs. 1–3. One can see that ω_+ and ω_- are clearly better indicators of the places where structure is most dominant, even for sample 3, where ω_1 and ω_p differ by 27%.

The fact that each reflectivity curve can be fit by a single plasma frequency and a constant plasmon lifetime is satisfying, but it is desirable that these parameters, especially ω_p, be obtained from independent measurements. In Table I we list the transport parameters, the plasma frequency, and lifetime calculated from transport parameters using values of m^* obtained from Faraday rotation measurements,[13] and the plasma frequency and lifetime obtained by fitting Eqs. (2)–(5) for our reflectivity spectra.

The small discrepancies in the values of ω_p and the larger discrepancies in τ when determined by transport

TABLE I. Transport properties and plasma parameters for doped n-GaAs at 78°K.

Sample No.	ρ ($10^{-3}\,\Omega$ cm)	R ($\text{cm}^{-3}\,C^{-1}$)	N[a] ($10^{17}\,\text{cm}^{-3}$)	μ_H[a] ($\text{cm}^2\,V^{-1}\,s^{-1}$)	m^*/m_e[b]	From R and ρ[c] ω_p ($10^{12}\,s^{-1}$)	From R and ρ[c] τ ($10^{-12}\,s$)	From reflectivity ω_p ($10^{12}\,s^{-1}$)	From reflectivity τ ($10^{-12}\,s$)
1	3.55	9.33	7.22	2433	0.0706	53.9	0.098	55.5	0.08
2	2.03	7.70	8.75	3495	0.0723	58.7	0.132	58.5	0.13
3	1.40	4.80	14.0	3174	0.0748	72.9	0.135	72.0	0.07

[a] Using $A = 1.08$.
[b] From DeMeis and Paul (Ref. 13) but scaling their values of N by 1.08 and of m^* by $(1.08)^{1/2}$.
[c] Using m^*/m_e from the preceding column.

and by optical methods are not important. τ may actually be smaller at infrared frequencies and cannot be determined to better than 10%. The fact that our values of τ do not increase monotonically as N decreases, contrary to expectation for ionized impurity scattering when only one type of impurity is present, is probably due to considerable compensation in our samples.

We can obtain values of m^*/m_e from the values of ω_p that fit the reflection spectra. For samples 1–3 at 78°K we find that m^*/m_e is 0.0668, 0.0726, and 0.0770, respectively. To compare these with the values of DeMeis and Paul[13] and of Spitzer and Whelan[12] one must increase them by about 4% to correct for the change in m^* due to increasing the temperature from 78 to 300°K.[13] To put our values on the same basis as those of Refs. 12 and 13 we must use $A=1$. The values of N in Table I must then be multiplied by $(1.08)^{-1}$ and the values of m^*/m_e listed above must be multiplied by $(1.08)^{-1/2}$, just cancelling the temperature correction. Our values of m^*/m_e thus "corrected" fall about 0.03 units below the data of Ref. 12, obtained by a method similar to ours, and range from 0.03 units below the data of Ref. 13 (sample 1) to about 0.05 units above them (sample 3). Agreement is "satisfactory," except for the unusually large dependence of m^*/m_e on N that we seem to have. This cannot be considered significant, however, because only three samples were used.

ACKNOWLEDGMENT

The advice and assistance of Dr. Joel L. Martin in the transport measurements is acknowledged.

PHYSICAL REVIEW VOLUME 177, NUMBER 3 15 JANUARY 1969

Two-Quantum Excitations in Alkali Halides*

J. C. HERMANSON

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 22 April 1968)

Optical excitations involving the simultaneous production of two or more excitons by a single photon in alkali halides are considered. The electron-electron interaction is approximated by a term derived from Toyozawa's theory of the electronic polaron. Using a Lee-Low-Pines transformation for the c.m. motion and the Hartree approximation for the internal motion of an exciton, dipole matrix elements are calculated for many-exciton transitions. Specifically, for typical alkali halides we find the oscillator strength ratio $f^{(2)}/f^{(1)}\sim 10^{-2}$, in disagreement with the ratio 1.5 obtained by Miyakawa for LiF. Ultraviolet and x-ray data in the two-exciton region are briefly discussed.

I. INTRODUCTION

THE optical properties of insulating solids (e.g., alkali halides[1,2] and rare-gas solids[3] have been extensively studied, both experimentally and theoretically, near the fundamental absorption edge.[4] For large-gap systems, the spectra are dominated by exciton absorption bands[5] above and below threshold. Structure at high energies has been identified with (1) Frenkel excitations[6] and charge transfer states,[7] (2) interband edges above the energy gap,[8] (3) metastable or "kinematic" exciton resonances,[9] (4) plasmon creation,[10] (5) core excitations,[11] and (6) two-exciton transitions[11,12] caused by electronic correlation. In this paper we present a calculation of contribution (6) to high-energy absorption in typical alkali halides, where the effects are expected to be most prominent.

Calculations of two-electron transitions have been

* Research supported in part by the Advanced Research Projects Agency under Contract No. SD-131.

[1] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959); F. Fischer and R. Hilsch, Z. Angew. Math. Phys. **8**, 241 (1959); K. J. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967); G. Baldini and B. Bosachi, *ibid.* **166**, 863 (1968); D. M. Roessler and W. C. Walker, J. Opt. Soc. Am. **57**, 677 (1967); Phys. Rev. **166**, 599 (1968); T. Miyata and T. Tomiki, J. Phys. Soc. Japan **22**, 209 (1967); **22**, 463 (1967).

[2] H. R. Phillipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

[3] O. Schnepp and K. Dressler, J. Chem. Phys. **33**, 49 (1960); G. Baldini, Phys. Rev. **128**, 1562 (1962); D. Beaglehole, Phys. Rev. Letters **15**, 551 (1965); J. F. O'Brien and K. J. Teegarden, *ibid.* **17**, 991 (1966).

[4] For a comprehensive review of the optical properties of solids, see J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[5] Exciton theory has been reviewed by R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

[6] D. L. Dexter, Phys. Rev. **83**, 435 (1951); **108**, 707 (1957); T. Muto, Y. Oyama, and H. Okuno, Progr. Theoret. Phys. (Kyoto) **20**, 804 (1958).

[7] R. Hilsch and R. W. Pohl, Z. Physik **57**, 145 (1929); **59**, 812 (1930); A. von Hippel, *ibid.* **101**, 1702 (1956); F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957); B. Goodman and O. S. Oen, J. Phys. Chem. Solids **8**, 291 (1959); R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[8] J. C. Phillips, Phys. Rev. **136**, A1705 (1964); **136**, A1714 (1964); **136**, A1721 (1964).

[9] M. Cardona and G. Harbeke, Phys. Rev. Letters **8**, 90 (1962); J. C. Phillips, *ibid.* **10**, 329 (1963); K. P. Jain, Phys. Rev. **139**, A544 (1965); J. Hermanson, Phys. Rev. Letters **18**, 170 (1967); Phys. Rev. **166**, 893 (1968).

[10] D. W. Lynch, Solid State Commun. **4**, 159 (1966).

[11] T. Miyakawa, J. Phys. Soc. Japan **17**, 1898 (1962).

[12] T. Sagawa *et al.*, J. Phys. Soc. Japan **21**, 2587 (1966).