Intrinsic Oscillatory Photoconductivity and the Band Structure of GaAs

Roger W. Shaw
Monsanto Company, St. Louis, Missouri 63166
(Received 12 October 1970)

Oscillations as a function of incident light energy are reported for the photoconductive response of high-purity epitaxial GaAs at 4.2 °K. The original report of Nahory is supplemented in several ways: As many as 15 oscillations are observed at low electric fields, corresponding to electron states 550 meV into the conduction band. These are approximately periodic with a period of 41.3 ± 0.3 meV, which yields a constant effective-mass ratio of $m_e/m_{hh} = 0.124 \pm 0.010$, where m_e and m_{hh} are the effective masses of the electron and heavy holes, respectively. As the field is raised above 0.5 V/cm, sample resistance gradually decreases owing to the growth of impact ionization of shallow donors. At the same time, the amplitude of the oscillations predominant at low field decreases while a longer-period oscillation remains relatively uneffected by the field increase. At 2 to 4 V/cm this oscillation dominates the photoresponse, displaying a period of approximately 82 meV. It is argued that these oscillations are due to light holes. This interpretation yields a mass ratio $m_{1h}/m_e = 1.22 \pm 0.02$ near the zone center and an increasing light-hole mass as k increases.

I. INTRODUCTION

Intrinsic oscillatory photoconductivity as a function of energy of the incident light was reported for GaAs by Nahory.[1] He observed approximately six oscillations beyond the band gap and related them to longitudinal optic (LO) phonon emission by electrons photoexcited from the heavy-hole band and to the effective-mass ratio m_e/m_{hh} via the equation

$$\Delta_{(e\text{-hh})} = \hbar\omega_{LO}(1 + m_e/m_{hh}) .$$

Here $\Delta_{(e\text{-hh})}$ is the period (in energy of the incident light) of the oscillations, $\hbar\omega_{LO}$ is the energy of the $k=0$ LO phonon equal to 36.75 meV, and m_e and m_{hh} are the effective masses of the electron and heavy holes, respectively.

We have studied this phenomenon on several samples of quality apparently superior to those available to Nahory. The new results are (i) the observation of as many as 15 oscillations which yield a more reliable value of the mass ratio m_e/m_{hh} and a look at the structure of the conduction band to $15\times\hbar\omega_{LO} = 550$ meV from the band edge and (ii) the observation that an increase of applied field to ~ 2 V/cm and the associated impact ionization of the shallow donors leads to suppression of the electron oscillations but leaves longer-period oscillations presumably due to both light and heavy holes. This permits a new determination of m_{1h}/m_e near the band edge and reflects the nonparabolicity of the light-hole band at higher photon energies.

II. EXPERIMENTAL

The measurements were made using a conventional tungsten source, grating monochromator, and 200-Hz chopper (the same effects were observed at dc). The light was conducted to the sample via a fiber optic light pipe allowing the sample wand to be simply immersed in a liquid-helium storage vessel at 4.2 °K, the temperature at which all of the measurements of this report were made. The 200-Hz sample response in a simple series circuit with a battery and resistor was detected with the aid of a lock-in amplifier. Part of the light output of the monochromator was conducted via an identical fiber optic to a PbS photoconductive cell with approximately flat response in the range of interest. The output of this cell was similarly detected and used to normalize the signal in an analog divider circuit. The data curves shown in Figs. 1 and 2 (see Sec. III) are recorder tracings of this normalized output.

The samples were grown by vapor-phase epitaxy on Cr-doped substrates and were not intentionally doped. Hall data for the three samples to be considered here are summarized in Table I.

III. RESULTS AND DISCUSSION

A. Low Electric Field

Figure 1(a) illustrates typical results for 0.5-V/cm or less applied field and resolution of 7 Å. A somewhat better signal-to-noise ratio could be

TABLE I. 77 °K Hall characteristics of samples reported.

Sample No.	Electron density (cm^{-3})	Hall mobility (cm^2/V sec)
971-5	4.2×10^{13}	133 000
962-3	9.0×10^{13}	80 700
959-5	4.0×10^{13}	108 000

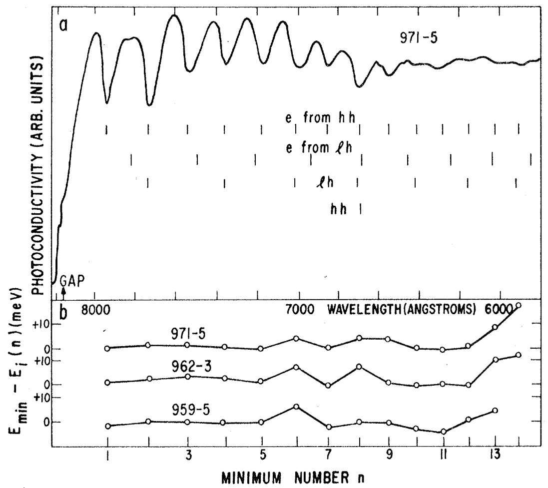

FIG. 1. (a) Normalized photoconductivity vs wavelength for sample 971-5 at 4.2 °K, 0.5-V/cm, and 7-Å resolution. Also shown are the positions of minima to be expected from various carriers on the basis of parabolic bands and LO phonon energy discussed in the text. (b) Deviations of the low-field minima from periodicity of 41.3 meV and zeroth minimum (band gap) of 1.520 eV. For convenience, the abscissas of Figs. 1(a) and 1(b) are actually the same wavelength scale.

achieved using the monochromator in second order without the electronic normalization and this was utilized in the analysis when needed. In the photoexcitation process in GaAs, electrons are raised from the heavy- and light-hole branches of the valence band (although because of the densities of states, the heavy-hole band predominates). Holes of both types are left and decay rapidly toward $k=0$ by emission of LO phonons as do the electrons. Competing decay processes are two or three orders of magnitude slower, so that the carrier photocurrent depends upon the state in which it is left when no further LO phonons can be emitted. Since the position $k=0$ corresponds to a minimum mobility and lifetime, starting points for the decay process which lead directly to $k=0$ will yield minimum photoconductivity.[2] The locations of the various minima expected from these processes are shown below the data curve in Fig. 1(a). For this purpose, the following values have been adopted: $m_e/m_{hh} = 0.124$ and $m_e/m_{1h} = 0.82$, corresponding closely to values in the literature,[3,4] and $\hbar\omega_{LO} = 36.75$ meV.[5] The basic oscillation is clearly due to electrons photoexcited from the heavy-hole band. Note, however, that the first minimum due to electrons from the light-hole band flattens the second maximum, and that the second minimum is unusually strong owing to concurrence with the first light-hole minimum. In addition, minimum number eight, for which all carriers return to $k=0$ almost simultaneously, is also strong. It should be realized that the return of holes to $k=0$ can lead to a minimum photoresponse in two ways: (a) via a minimum in the photocurrent carried by the holes, and (b) via a minimum in the *electron* photocurrent by causing a reduction in the lifetime of electrons. This latter mechanism will be of considerable importance in Sec. III B.

Figure 1(b) shows details of the energies at which the minima occur for three samples. Here $E_i(n) = 1.520 + 0.0413n$ eV, the energies of the minima expected for a gap of 1.520 eV and a period of 41.3 meV. It is clear from the figure that this period is approximately valid out to $n = 12$ (440 meV into the conduction band). The systematic variation at $n = 6$ (the last minimum shown by Nahory[1]) probably results from the combination of minima associated with electrons excited from both valence bands and one associated with light holes. It would appear from these measurements that, in the range from the energy gap to $n = 12$, there is no evidence of a monotonic deviation from parabolicity of the conduction band or the heavy-hole band and that $m_e/m_{hh} = 0.124 \pm 0.010$ (corresponding to the observed oscillation period 41.3 ± 0.3 meV). Assuming $m_e = 0.067m$,[3] this result yields a value of $m_{hh}/m = 0.54 \pm 0.04$, to be compared with other recent values ranging between 0.45 and 0.50.[3,4]

Both doping[6-8] and magneto-optical measurements[3] indicate an increase in effective mass as k increases in the range covered here. This disagreement with the present result is probably due to anisotropy in the conduction band which effects the various experiments differently. Other alternatives, such as distortion of the bands in the other experiments or compensating bending of the heavy-hole valence band, appear to be less likely. If we assume that the heavy-hole band is strictly parabolic for 55 meV from its edge, then the present results indicate that the largest regions of approximately spherical constant-energy contours in the conduction band correspond to the same effective mass which predominates near the band edge.

B. Higher Electric Fields

Figure 2 illustrates the effect of increased electric field on the oscillations. In the range shown, impact ionization of shallow donors is increasing and the electron oscillations gradually disappear.[9] It is clear that another type of oscillation remains, and that these oscillations have approximately twice the period of the electron oscillations. Just such a period is to be expected from light holes, as can be seen from the minima positions for these carriers indicated in Fig. 1(a). In addition, note that the minimum near 6700 Å is quite strong,

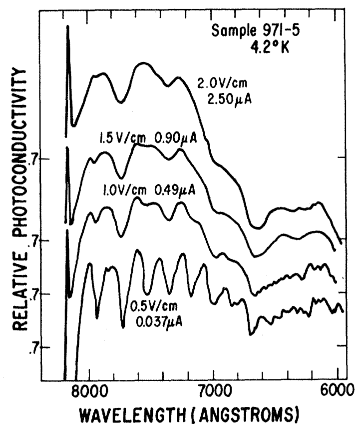

FIG. 2. Photoconductivity vs wavelength showing the variation with electric field and current. Curves have been normalized to unity at 7600 Å and displaced vertically for clarity.

as would be expected if heavy holes were also contributing to the oscillations at 2 V/cm. We take these two observations to be sufficient justification for assigning the minima observed at 2 V/cm to the return of holes of both types to $k=0$. Because the electron mobility is considerably larger than the hole mobility in GaAs, it is likely that the influence of the holes is felt primarily through a decrease in the electron lifetime when holes return to $k=0$. As far as is known, this is the first observation of such a hole-dominated oscillation in photoconductivity.

While models for the effect of field on the oscillations are not far enough advanced to add much strength to the above assignment, it is interesting to take this assignment and follow its implications briefly. The electron concentration in this sample at 2 V/cm and 4.2 °K is approximately $10^{12}/cm^3$. This appears to be too low to significantly alter the ionized impurity scattering or contribute measurable electron-electron scattering. Thus the photoexcited electrons are left in the same state after LO phonon cascade as they were at lower fields and their scattering is largely unchanged. What has changed is the choice of decay channels open to them after LO phonon cascade, the holes needed for recombination being largely consumed by the electrons created by impact ionization. If the availability of holes were basic to the dominant mechanism by which electrons are removed from the conduction band at low fields, the lack of holes after impact ionization sets in would give the electrons time to thermalize and the electron oscillations would wash out, as is observed. It appears unlikely that the explanation for field quenching of oscillations advanced by Stocker *et al.*[2] for InSb at higher fields is applicable here. We propose, then, that competition between photoexcited and impact-excited electrons for the fast recombination process in which holes play a central role is basic to quenching of the electron oscillations. Examples of such processes would include exciton formation and electron trapping on neutral acceptors.

Figure 2 also shows a sharp peak in photoconductivity at approximately 8170 Å. At higher resolution, this peak exhibits structure similar to that reported by Shah *et al.*[10] and is attributed by them to exciton creation followed by Auger decay leading to the creation of free carriers. The growth of the peak in Fig. 2 with increasing field is probably the result of impact breakup of the excitons. This phenomenon is under further investigation.

Both samples 971-5 and 962-3 showed the long-period oscillation clearly, while 959-5 tended toward negative differential resistance earlier and was thus difficult to use. The best signal-to-noise ratios were achieved in second order of the spectrometer where electronic normalization was inconvenient. One recorder tracing in second order is shown in Fig. 3 for each of the samples which clearly displayed the long-period oscillation. The light intensity vs wavelength as measured at comparable slit widths using room-temperature GaAs and silicon detectors is shown in the dashed curve. It is clear that the agreement between these two samples, with regard both to minima positions and general curve shape, is excellent.

The results of 12 passes on 971-5 and 962-3

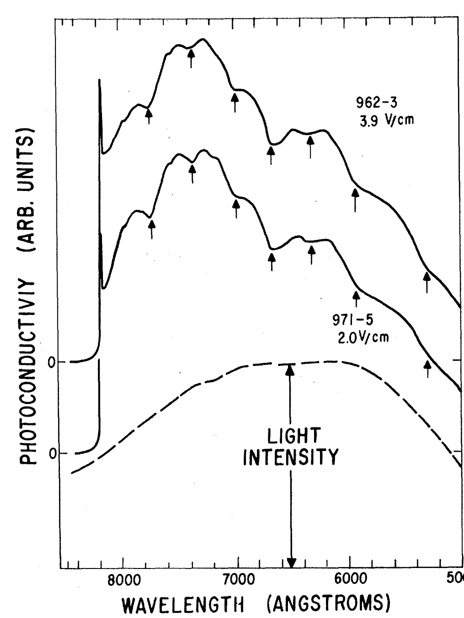

FIG. 3. Unnormalized photoconductivity vs wavelength under optimum conditions for observation of the longer-period oscillation. Variation in light intensity with wavelength is shown by the dashed curve.

samples at various biases, resolutions, and grating orders are summarized in Table II. Near the band edge, the period was approximately constant at 81.5 ± 1.0. The equation $\Delta_{(1h-e)} = \hbar\omega_{LO}(1 + m_{1h}/m_e)$ then yields $m_{1h}/m_e = 1.22 \pm 0.02$. Taking $m_e = 0.067m$, we find $m_{1h} = 0.082 \pm 0.002$, in excellent agreement with Vrehen[3] and other references quoted therein. The third and later periods become progressively larger (with the exception of number 4, which is complicated by the first minimum owing to heavy holes). These longer periods result from flattening of the light-hole band which requires the electrons from the light-hole band to be lifted further into the conduction band before the resultant holes have sufficient energy to give off an additional LO phonon. Using the results from the low-field measurements above which indicate that the conduction band is basically parabolic to 440 meV and assuming it to be described by $m_e = 0.067m$, we can construct the light-hole band, as averaged over all directions by the measurement. The result is shown in Fig. 4, where the last minimum has been excluded on the grounds that conduction-band states are involved for which the constant-effective-mass assumption has no basis. Deviations from parabolicity are evident and are quite precise, the uncertainties in k resulting from those shown for $h\nu_{min}$ in Table II being less than the size of the points.

In comparing this result with the theory of Kane[11] and more recent band calculations,[12,13] it should be kept in mind that these theories indicate the largest deviations from parabolicity are anisotropic. For example, neglecting interactions with bands above the conduction and below the split-off valence band, Kane finds this light-hole band to be parabolic along ⟨100⟩ directions. Thus the present results probably reflect the properties of relatively large regions of k space in lower-symmetry directions which have approximately spherical constant-energy contours. Possible contributions to the present oscillations from the split-off valence band have been neglected here because neither the onset of band-to-band transitions nor the first minimum, to be expected at 6250 and 6670 Å, respectively,[14] are discernible in the data. Similarly, no structure attributable to the higher minima of the conduction band has been observed.

TABLE II. Average values for long-period oscillations in photoconductivity.

	Minimum number	$h\nu_{min}$ (eV)	RMS deviation (meV)	$\Delta_{(1h-e)}$ (meV)
(Band gap)	0	(1.520)	...	...
	1	1.602	±1	82
	2	1.683	±2	81
	3	1.771	±1	88
	4	1.858	±2	87
	5	1.960	±4	102
	6	2.095	±4	135
	7	2.335	±4	240

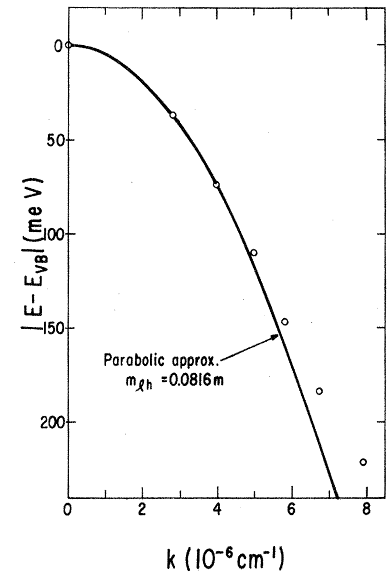

FIG. 4. Energy vs wave-vector magnitude for the light-hole band as indicated by the long-period oscillations at higher fields where E is the energy of the hole state and E_{VB} is the energy of the valence band edge. A basically parabolic conduction band out to these k values is assumed as discussed in the text.

IV. CONCLUSIONS

From the oscillatory photoconductivity measurements at low electric fields and assuming a parabolic heavy-hole band, we conclude that the conduction band of GaAs has substantial sections which are parabolic up to 440 meV and which are described by $m_e/m_{hh} = 0.124 \pm 0.010$. At higher electric fields (~ 2 V/cm), impact ionization of shallow donors occurs and the electron oscillations disappear in the purest samples leaving those due to light and heavy holes. Near the band gap, these yield $m_{1h}/m_e = 1.22 \pm 0.02$ and deeper in the band indicate an increasing light-hole mass. The one observed minimum due to heavy holes is in agreement with the above m_e/m_{hh} ratio.

ACKNOWLEDGMENTS

The excellent samples used in this work were grown by Dr. R. E. Walline, for which it is a pleasure to thank him. The author also gratefully acknowledges valuable discussions with Dr. D. E. Hill and Dr. P. T. Bailey and the technical assistance of R. D. Fowler.

[1]R. E. Nahory, Phys. Rev. 178, 1293 (1969).

[2]These processes have been discussed by H. J. Stocker and H. Kaplan, Phys. Rev. 150, 619 (1966); and experimental work prior to mid-1966 was summarized by H. J. Stocker, H. Levinstein, and C. R. Stannard, *ibid.* 150, 613 (1966).

[3]Q. H. F. Vrehen, J. Phys. Chem. Solids 29, 129 (1968).

[4]A. K. Walton and U. K. Mishra, J. Phys. C 1, 533 (1968).

[5]A. Mooradian and G. B. Wright, Solid State Commun. 4, 431 (1966).

[6]M. Cardona, Phys. Rev. 121, 752 (1961).

[7]H. Ehrenreich, Phys. Rev. 120, 1951 (1960).

[8]C. G. Olson and D. W. Lynch, Phys. Rev. 177, 1231 (1969).

[9]Similar effects in p-type InSb were studied in Ref. 2.

[10]J. Shah, R. C. C. Leite, and R. E. Nahory, Phys. Rev. 184, 811 (1969).

[11]E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[12]K. Kreher, Fortschr. Physik 12, 489 (1964).

[13]R. L. Bowers and G. D. Mahan, Phys. Rev. 185, 1073 (1969).

[14]M. Reine, R. L. Aggarwal, B. Lax, and C. M. Wolfe, Phys. Rev. B 2, 458 (1970).

PHYSICAL REVIEW B VOLUME 3, NUMBER 10 15 MAY 1971

Electron Transport in InSb, InAs, and InP

D. L. Rode
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 15 December 1970)

The calculation of electron-transport properties of direct-gap semiconductors has been generalized to include arbitrary electron degeneracy as well as scattering by ionized impurities and heavy holes. Conduction-band nonparabolicity and electron wave-function admixture are retained throughout the calculation of drift mobility and thermoelectric power. Extensive comparison of the results with experiment confirms the present description over wide ranges of temperature and ionized-impurity concentration. Effects of multivalley conduction due to electron transfer into L_{1c} satellite valleys appear in InSb above 700 °K (just below the melting point at ~780 °K) and in InP above 800 °K. The lowest satellite valleys of InAs are sufficiently remote from the conduction-band edge at Γ_{1c} that the results are expected to be accurate up to the melting point at ~1200 °K.

I. INTRODUCTION

Transport properties of electrons in direct-gap semiconductors can be conveniently derived by direct solution of the Boltzmann equation. Previous applications[1,2] of this technique were directed toward calculations of drift mobility in ideally pure semiconductors. There is also considerable interest in accurate descriptions of impure crystals, from both the experimental and the theoretical points of view. In the former case, for example, one may take advantage of the sensitivity of mobility to ionized impurities in analyses of impurity content.[3] In the latter case, highly doped materials allow one to probe regions of the conduction band in the neighborhood of the Fermi level, well above the band edge. Obviously, accurate calculations in conjunction with experimental data are helpful in exposing weaknesses of the theoretical model, particularly with regard to electron scattering by ionized impurities at low temperatures.[4]

The purpose of the present paper is to calculate electron-drift mobility and thermoelectric power for various temperatures and ionized-impurity concentrations. The formulation itself applies only to conduction in the single Γ_{1c} minimum of direct-gap semiconductors; detailed comparison of the results with experiment helps to indicate the onset of multivalley conduction. Only in the extremes of high temperature or high free-electron concentration do multivalley effects become evident. For the remaining broad range of temperature and impurity concentration, the formulation presented in Sec. II will be seen to agree well with experiment in a *quantitative* as well as qualitative fashion.

In order to allow for wide ranges of temperature and electron concentration, it is necessary to generalize the earlier treatment[1] to include electron degeneracy and scattering by ionized impurities and holes. The appropriate formulation of the Boltzmann equation for Fermi-Dirac statistics is developed in Sec. II. Perturbation from equilibrium by a small electric field or temperature gradient leads to a linear-difference equation for the perturbed part of the distribution function.[5,6] The effects of electron scattering are *formally* included in the difference equation. In Sec. III, the following scattering processes are evaluated explicitly: (i) piezoelectric scattering[7,8] by transverse and longitudinal acoustic modes, (ii) deformation-potential