

mentally easily achievable. But all other parameters remain unknown. One gains, therefore, no significant information on the kinetical process by studying TL, TSC, or TSC-TL correlations alone. It appears even doubtful whether a consistent value obtained for E is of relevance, since there seems to be no way to check the applicability of the simple basic model for a particular crystal by measuring and analyzing TSC and TL glow curves. Other conceivable models must be investigated, e.g., those which consider two activation energies.^{6,23,24} By looking at those models, it appears questionable if the initial rise of a glow curve is always determined solely by the depth of a trap. Detailed investigations of some of the more relevant models are needed

²³ P. Bräunlich, *Ann. Physik* **12**, 262 (1963).

²⁴ P. Bräunlich, *J. Appl. Phys.* **39**, 2953 (1968).

and will be presented in a later paper, with the goal to answer these questions.

We conclude that TSC and TL experiments are not adequate tools for measuring trapping parameters in contrast to statements on the subject in the literature. Isolated experiments on glow curves are of little value unless the pertinent parameters are measured by some other experimental technique, in which case TL and TSC may provide an excellent means of checking the results.

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Far-Infrared Donor Absorption and Photoconductivity in Epitaxial n -Type GaAs

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Donor-state absorption and photoconductivity spectra of n -type epitaxial GaAs layers with carrier concentrations in the range 10^{14} – 10^{16} /cm³ are reported. The essentially effective-mass-like behavior of the impurity spectra is confirmed, and ionization energies of 6.08, 5.81, 5.89, and 6.10 ± 0.025 meV are reported for Ge, Si, Se, and S donors. The influence of impurity-banding upon the values of E_D is considered. Central-cell corrections to donor ground-state energies are discussed.

THE effective mass of an electron in the $\mathbf{k}=0$ minimum of the conduction band of GaAs has recently been reported as $(0.0665 \pm 0.0005)m_0$.¹ The binding energy E_H predicted by effective-mass theory for the ground state of a simple donor near $\mathbf{k}=0$ will, therefore, be small, $E_H=5.79$ meV.² Many older estimates of donor binding energies, based mainly upon electrical measurements of fairly impure bulk-grown

material, are in the region of 2–5 meV.³ As it is difficult to envisage a potential field that will produce such shallow isolated donors in a III-V semiconductor, it is highly probable that these estimates are influenced by donor-impurity banding.

Epitaxial growth techniques now produce GaAs layers of a purity not previously available, and thus it is of interest to investigate by direct means the question of donor binding energies in n -type GaAs. Very recently, spectroscopic determinations of donor ionization energies E_D of 4.6,⁴ ~ 5.1 ,⁵ 6.8,⁶ 6.0,⁷ and ~ 6.5 meV⁸ have been reported. Direct chemical identifications have not

¹ G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, *Solid State Commun.* **7**, 921 (1969).

² The measurement of ϵ_0 in GaAs seems to have posed several problems and consistent values are simply not available. [See low-frequency determinations reported for ϵ_0 ; K. S. Champlin *et al.*, *Appl. Phys. Letters* **11**, 348 (1967); N. Braslau, *ibid.* **11**, 350 (1967); S. Jones and S. Mao, *ibid.* **11**, 351 (1967); C. B. Rodgers *et al.*, *ibid.* **11**, 353 (1967). We reverse the procedure by noting that our result for Si in GaAs puts an upper limit on E_H , and therefore, a (lower) bounded value on ϵ_0 . This bounded value is in good agreement with a room-temperature static determination of 12.5 ± 0.3 for ϵ_0 . We have thus used $\epsilon_0=12.5$ and $m^*=0.0665 \pm 0.0005$ as the most consistent and best values available to calculate the hydrogenic donor binding energy in GaAs. We obtain $E_H=13.6m^*/\epsilon_0^2=5.79 \pm 0.28$ meV.

³ S. M. Sze and J. C. Irvin, *Solid State Electron.* **11**, 599 (1968).

⁴ D. R. Bosomworth, R. S. Crandall, and R. E. Enstrom, *Phys. Letters* **28A**, 320 (1968).

⁵ J. Shah, R. C. C. Leite, and J. P. Gordon, *Phys. Rev.* **176**, 938 (1968).

⁶ E. H. Borgardus and H. B. Bebb, *Phys. Rev.* **176**, 993 (1968).

⁷ M. A. Gillo, P. T. Bailey, and D. E. Hill, *Phys. Rev.* **174**, 898 (1968).

⁸ R. Dingle, *Phys. Rev.* **184**, 788 (1969).

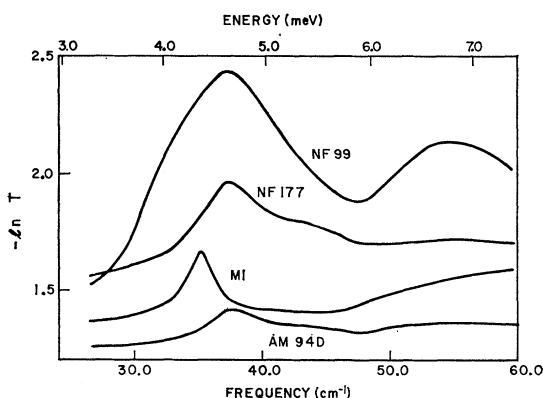


FIG. 1. Donor-state absorption spectra for epitaxial *n*-type GaAs at 4.2°K.

been made, although silicon and selenium have been suggested as possible contaminants.

In this paper, we present measurements of the far-infrared absorption and photoconductivity spectrum of epitaxial layers of *n*-type GaAs between 20 and 70 cm^{-1} . The results confirm the effective-mass-like behavior of donors in high-purity material. Furthermore, by use of suitably doped samples, various donors have been identified and approximate central-cell corrections established. The latter appear to be consistent with a recent theory proposed by Phillips.⁹

EXPERIMENTAL

The infrared measurements were made at 4.2°K using a Beckman RIIC FS720 interferometric spectrometer. Frequencies greater than 80 cm^{-1} were blocked by using a Beckman number one filter and black polyethylene. Spectra were taken at a resolution of 1 cm^{-1} and computed in a manner similar to that described by Bosomworth and Gush.¹⁰ The spectra shown are the average of several runs. For the photoconductivity work, Ohmic contacts were formed by alloying with tin or indium. Samples were biased by approximately 1 V, and had dark current resistivities between 0.5 and 44 M Ω at 4.2°K. All samples were grown on substrates of high resistivity, bulk GaAs doped with chromium. When wedged, the substrates showed no absorption bands in the region 15–100 cm^{-1} . Table I summarizes the physical and chemical properties of each sample.

Samples NF 177, NF 99, and AM94D were grown at Bell Telephone Laboratories by an AsCl_3 -Ga- H_2 vapor-transport method. Without the deliberate introduction of Ge as a dopant, the system produced either *p*-type layers with hole concentrations $\approx 10^{13}/\text{cc}$, or high-resistivity material. Doping was accomplished by transporting Ge from a gallium source that had been

doped with GeH_4 . *n*-type layers with free carriers in the range 10^{15} – $10^{18}/\text{cm}^3$ could be produced in this manner. Mass spectrographic analysis of the layers produced by this technique showed Ge as the major impurity from groups IV and VI in the crystal.

The *M* series of samples were grown at the Monsanto Company by a similar vapor-transport method. The sulfur and selenium doping was achieved using H_2S and H_2Se , respectively, with growth conditions such that layers grown without the presence of the doping gas had carrier concentrations at least ten times smaller than the desired doping level. The specimen we have designated as silicon doped was grown under different conditions such that the layers grown without deliberate doping had carrier concentrations in the 10^{14} – $10^{15}/\text{cm}^3$ range. Because of the considerable quantity of fused silica in the growth apparatus, including the enclosing tube which is maintained at the growth temperature, we believe silicon to be the most likely impurity present in these layers.

High-resolution photoluminescence spectra in the near band-gap region give some confirmation to these identifications. Gilleo, Bailey, and Hill (Ref. 7 and further unpublished work) find that the main line, which is due to an exciton decaying at a neutral donor, is at higher energies in the undoped samples than it is in the Se-doped layers. This is consistent with the values of $E_{D_s}^*$ which we propose for Si and Se in this paper. In the case of the amphoteric impurities Ge and Si, we also identify characteristic donor-acceptor pair spectra with the presence of Ge and Si acceptors in these doped layers. Layers not doped with these impurities do not show such spectra.

RESULT: INFRARED ABSORPTION AND PHOTOCONDUCTIVITY

A plot of $-\log$ transmission of the substrate and layer is shown as a function of frequency for several representative samples in Fig. 1. The photoconductivity response as a function of frequency is shown in Fig. 2. All spectra have been corrected for the response of the instrument.

TABLE I. Physical and electrical properties of specimens at 300 and 77°K.

Sample	Temp. (°K)	$N_D - N_A / \text{cc}$	μ (cm/V sec)	d (μ)	Dopant
NF 177	300	7.7×10^{14}	7 500	40	Ge
	77	7.7×10^{14}	48 000		
AM 94D	300	2.2×10^{15}	7 100	11.2	Ge
	77	1.9×10^{15}	30 000		
NF 99	300	1.9×10^{15}	6 640	65	Ge
	77				
M1	300	1×10^{15}	6 300	20.5	Si
	77	9×10^{14}	80 000		
M2	300	2.2×10^{14}	6 560	24	Se
	77				
M3	300	2.9×10^{14}	8 250	4.5	S
	77		50 000		

⁹ J. C. Phillips, Phys. Rev. (to be published).

¹⁰ D. R. Bosomworth and H. P. Gush, Can. J. Phys. 43, 729 (1965).

From Figs. 1 and 2 and Table I, it is seen that the quality of the spectrum depends on having samples of low carrier concentration and high mobility. The absorption spectrum of sample NF 177 shows the most distinctive features. A strong absorption band is observed at $37.4 \pm 0.2 \text{ cm}^{-1}$, a shoulder near 44 cm^{-1} , and what may be the photoionization threshold at $\sim 48 \text{ cm}^{-1}$. Measurements on samples AM94D and NF 99 confirm these features and strengthen our belief that the increase in absorption at $\sim 48 \text{ cm}^{-1}$ marks the photoionization threshold. We associate the lowest-energy feature in the absorption spectrum with a transition from the $n=1$ ground state of a hydrogenic donor to its first ($n=2$) excited state. This association is confirmed by the better resolved spectrum obtained from very high-purity epitaxial layers by Stillman *et al.*¹ (Note that the $1s-2p$ peak is not at exactly the same energy in the two investigations.) Our assignment is consistent with the effective-mass theory of hydrogenic donors in GaAs if one assumes a positive central-cell correction E_D-E_H of $+0.29 \text{ meV}$ for the germanium donor on a gallium site. Sample M1, which is doped with silicon, shows a strong absorption band at $35.2 \pm 0.2 \text{ cm}^{-1}$ (in close agreement with the results of Stillman *et al.*¹). These features are confirmed by the photoconductivity spectrum of M1 shown in Fig. 2.

By using $m^* = 0.0665$,¹ $\epsilon_0 = 12.5$,¹¹ the $2p$ -ionization threshold separation given by the hydrogenic model, and the experimentally determined $1s-2p$ separations, we have derived the ionization energies and central-cell corrections reported in Table II. This analysis leads to the conclusion that (a) all four donor defects studied have nearly effective-mass binding energies, and (b) the central-cell corrections are positive.

DISCUSSION

The experimental results provide a basis for the argument that isolated-donor binding energies in high-purity GaAs are similar to, but slightly greater than that predicted by the hydrogenic model. Although this is not a surprising statement, it is contrary to many

TABLE II. Transition energies and E_D-E_H as determined from absorption and photoconductivity results.

Sample	E_D-E_H (meV)	$n=1 \rightarrow n=2$ cm^{-1}	$n=1 \rightarrow \text{C.B.}$ $E_D \text{ cm}^{-1}$	Donor
E.M.A.	...	35.0 cm^{-1} (4.34 meV)	46.7 cm^{-1} (5.788 meV)	...
NF 177	0.29	37.4 ± 0.2	48.0 ± 1.0	Ge
AM 94D	0.29	37.3 ± 0.2	48.2 ± 0.5	Ge
NF 99	0.29	37.4 ± 0.2	48.2 ± 0.5	Ge
M1	0.02	35.2 ± 0.2	46.5 ± 0.5	Si
		35.2 ± 0.2	46.5 ± 0.5	
M2 ^a	0.10	35.9 ± 0.2	47 ± 0.5	Se
M3 ^a	0.31	37.5 ± 1	...	S

^a Photoconductivity results.

¹¹ O. Madeling, in *Physics of III-V Compounds* (J. Wiley & Sons, Inc., New York, 1964).

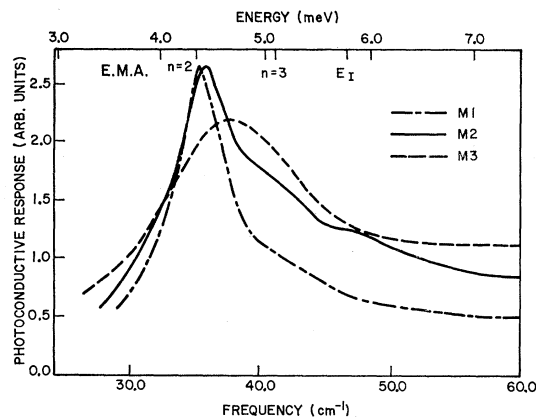


FIG. 2. Far-infrared photoconductivity in n -type epitaxial GaAs at 4.2°K .

reports found in the literature. Below we consider the influence of donor concentration upon the isolated donor energy levels and upon the value of E_D as derived from diverse experimental techniques. In dealing with these points, we produce explanations for some of the values of E_D found in the literature. Finally, the question of the central-cell corrections associated with shallow donors in GaAs is considered.

For impurity states in a crystal, Mott¹² has defined a broadening parameter $\beta = \alpha N_D^{1/3}$, where α is the Bohr radius of the energy state in question, and N_D is the total donor concentration per cm^3 . Interdonor interaction and the accompanying broadening of energy levels is expected whenever $\beta > 0.25$. Values of β pertinent to the present discussion are shown in Table III.

The spectral resolution of the infrared (IR) spectra is very dependent on the banding of the $n=2, n=3, \dots$ states. The photoconductivity and electrical measurements (Hall, ionization data) are likewise locked to the degree of interdonor interaction and to the merging of the excited donor states with the conduction band. It is clear from Table III that only material of the highest purity $N_D \leq 1 \times 10^{14}$ can escape this banding in the $n=2$ state. The breadth of the first peak in Figs. 1 and 2 is consistent with this point of view, and the $\sim 5 \text{ cm}^{-1}$ half-widths are primarily due to this impurity banding effect.

The higher excited states of the donor will certainly form bands and overlap the conduction band, thereby giving rise to a well-defined tail band for electrical conduction in material where $N_D > 10^{14}/\text{cc}$. Hall-effect measurements by Whitaker and Bolger¹³ confirm this conclusion. We observe effective ionization energies (from the $n=1$ level to the bottom of the $n=2$ band) of 3.8 ($N_D-N_A = 2.2 \times 10^{14}/\text{cm}^3$), 3.6 ($2 \times 10^{15}/\text{cm}^3$), and 3.1 meV ($8.5 \times 10^{15}/\text{cm}^3$, not shown in figure) in reasonable agreement with the electrical data.

¹² N. F. Mott, *Phil. Mag.* **6**, 287 (1961).

¹³ J. Whitaker and D. E. Bolger, *Solid State Commun.* **4**, 181 (1966).

TABLE III. Mott's broadening parameter β for donor states in GaAs as a function of donor concentration.^a

N_D/cc	β ($n=1$), <i>s</i>	β ($n=2$), <i>p</i>	β ($n=3$), <i>p</i>
5×10^{16}	0.368	1.47	...
1×10^{16}	0.215	0.86	...
1×10^{15}	0.100	0.40	0.90
1×10^{14}	0.0465	0.186	0.418
1×10^{13}	0.0215	0.086	0.194

^a The Bohr radius of the ground state is $a_H = a_{\text{Bohr}}(\epsilon_0/m^*) \approx 100 \text{ \AA}$. The *s*- and *p*-like states are indicated. In the italicized part of the table, isolated-donor states are likely; above it, impurity banding occurs.

Time-resolved donor-acceptor pair spectra taken at *low* temperatures give rise to donor and acceptor binding energies that are independent of the banding in the $n=2$ donor state, as it is only the Bohr radius of the $n=1$ donor state that is important in this technique. Thus, for material where $N_D \leq 10^{16}/\text{cm}^3$ (Table II), good approximations to isolated donor ionization energies are obtained. We find $E_D = 6.5 \pm 1.0$ meV for $N_D \approx 5 \times 10^{15}/\text{cm}^3$.

In summation, we feel that it has been demonstrated that donor binding energies in GaAs are equal to or greater than the effective-mass value, and that the smaller values found in the literature can be satisfactorily explained as the result of impurity banding in the $n > 1$ donor states. Furthermore, our results clearly indicate that the donor binding energy is not given exactly by the simple hydrogenic model¹ and that central-cell corrections must be considered.

The positive central-cell corrections reported (Table II) are thought to be real and not influenced by the donor concentration of the samples measured [see results for germanium donors (Fig. 1)]. The spectra for sample M3 were rather noisy; thus the value of $E_D - E_H$ for the sulfur donor in Table II is a tentative one.

The deviations from the hydrogenic model are small [$(E_D - E_H)/E_H \sim 0.05$], in contrast to these reported for donor impurities in germanium, silicon,¹⁴ and gallium phosphide¹⁵ [$(E_D - E_H)/E_H \sim 1$]. In general terms, these differences are to be expected, since the probability of finding the donor electron in the central cell is

$P_H = \frac{1}{4}a^3|\psi_0|^2$ per conduction-band minimum (a is the lattice constant and ψ_0 is the ground-state wave function in the central cell). Taking into account the ground-state Bohr radii, which are $\sim 100, 45, 20$, and 17 \AA for GaAs, Ge, Si, and GaP, respectively, one finds average experimental central-cell corrections⁹ that are consistent with this expectation.

Phillips⁹ has recently proposed a dielectric theory of impurity binding energies, which he has applied to donors in the indirect-gap semiconductors Ge, Si, and GaP. In heteropolar crystals the deviations from the effective-mass binding energy are accounted for by two dominant mechanisms. These are (1) a homopolar term which results from the change in the valence energy due to mismatch of valence bands between the impurity atom and the neighboring host atoms and (2) a heteropolar contribution arising from the residual ionic charge on each atom in the unit cell. Both of these contributions depend directly upon P_H .

Phillips has shown that the heteropolar contributions dominate the homopolar terms in GaP. In GaAs, which is a more covalent crystal than GaP, one might expect that homopolar contributions would be more important than in GaP. Any attempt at a quantitative evaluation of our data is prevented by the fact that the error associated with m^* and ϵ_0 (which are used to find the hydrogenic donor binding energy), is large, and the experimental variations are small. If $E_H = 5.79$ meV is valid, then for S and Se donors the deviations from E_H are in the correct⁹ order, i.e., $S > \text{Se}$, and of a magnitude that suggests the homopolar contribution to be more important than in GaP. The results for Si give the closest agreement with the hydrogenic value. This result, and the difference between Si and Ge donors are consistent with the homopolar contributions outlined by Phillips.⁹

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¹⁴ W. Kohn, *Solid State Phys.* **5**, 257 (1957).

¹⁵ Values quoted in Ref. 9.