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Effect of Stress on the Electrical Properties of *n*-Type Gallium Arsenide*

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The electrical resistivity and Hall coefficient of undoped *n*-type GaAs samples with room-temperature carrier concentrations between 1.9×10^{14} cm^{-3} and 3.7×10^{16} cm^{-3} have been measured as a function of uniaxial compression (up to 2×10^{8} dyn/cm^2) at various temperatures between 77 and 298°K and as a function of hydrostatic pressure (up to 6×10^{9} dyn/cm^2) between 195 and 298°K. Some measurements were also made on two vanadium-doped samples. The results indicate that conduction takes place in a single band at $\mathbf{k}=0$ and that the concentration n and mobility μ of the carriers in this band decrease with increasing compressional stress, the rate of decrease of n being much greater than that of μ in some cases. Between 195 and 298°K the conduction-electron concentration is explained quantitatively by the presence of nonshallow donors having a pressure-dependent ionization energy $E_I\approx[0.17+10^{-11}P_{\mathrm{dyn/cm^2}}]$ eV, as well as of shallow donors and acceptors. At lower temperatures the stress dependence of n cannot be explained using the above nonshallow level but seems to imply the presence of a less deep, nonshallow level. The dependence of the mobility on pressure is accounted for in most cases by the variation of the electron effective mass with pressure. Impurity-level concentrations deduced from the electrical measurements, the nature of the nonshallow donors, and the role of vanadium impurity are discussed with the aid of mass-spectrographic analyses. Carbon, nitrogen, and oxygen seem to be likely sources of the 0.17-eV donor levels.

I. INTRODUCTION

PREVIOUS piezoresistance measurements on *n*-type GaAs have been made near 300°K by various investigators.[1–3] Of these Sagar,[1] employing uniaxial stress or hydrostatic pressure, and Zerbst,[3] employing uniaxial stress, found that all components of the piezoresistance tensor were small. Each interpreted his results to mean that there was no appreciable transfer of electrons between minima made nonequivalent by uniaxial stress[4] and thus that conduction must be via electrons in a band centered at $\mathbf{k}=0$.

Howard and Paul[2] employing hydrostatic pressures up to 30 kbar (compared to a maximum of 13 kbar by Sagar) found, as did Sagar, that at low pressures the resistivity increased linearly with increasing pressure, the rate of increase being small. This behavior was attributed to the mobility of the $\mathbf{k}=0$ band varying inversely with pressure because of the effective mass increasing with pressure.[5] Above 10 kbar both groups found that the rate of change of resistivity increased gradually with pressure. Above 20 kbar Howard and Paul[2] observed a very steep increase of resistance with pressure, and Howard[2] found that at still higher (nonhydrostatic) pressures the resistivity reached a plateau. The results above 10 kbar were interpreted as due to conduction in a second band of lower mobility becoming of increasing importance as this band moves down relative to the $\mathbf{k}=0$ band as the pressure is increased[5] until finally all carriers are in the low mobility band.[2] This low mobility band was taken to be a band comprised of (100) minima because the separation of such a band from the $\mathbf{k}=0$ band has an appropriate pressure dependence.[2]

Some magnetoresistance measurements[6,7] on *n*-GaAs, are also consistent with conduction being in a $\mathbf{k}=0$ band only (at zero applied pressure). However, other measurements have revealed magnetoresistance anisotropy.[6,8,9] Although the anisotropy was deemed spurious (due to contact effects) in one investigation,[6] it was not deemed so in a recent detailed investigation.[9] Instead, the anisotropy was attributed to there being appreciable conduction by electrons in (100)-type minima as well as in the band at $\mathbf{k}=0$.[9] This required that the (100) minima be much closer to the $\mathbf{k}=0$ band than indicated by other evidence,[5] including the piezoresistance data summarized above.

Since the magnetoresistance effects which were attributed to appreciable conduction in (100) minima were particularly evident in samples of lower carrier concentration than used in the earlier magnetoresistance measurements, or in previous piezoresistance measurements, we decided to make piezoresistance measurements on samples having relatively small carrier concentrations. Our initial results using uniaxial compression[10] indicated larger piezoresistance at low stresses than observed previously on less pure samples.[1,3] This could not be attributed to electron transfer effects, nor to less carrier degeneracy, and we extended the investigation in order to learn the reason. The extension consisted of making Hall effect, as well as resistance, measurements as a function of hydrostatic pressure

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[2] W. Paul, J. Appl. Phys. **32**, 2082 (1961).

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[8] J. T. Edmond, R. F. Broom, and F. A. Cunnell, *Report of the Meeting on Semiconductors, Rugby 1956* (The Physical Society, London), p. 109.

[9] A. F. Kravchenko and H. Y. Fan, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962* (Institute of Physics and the Physical Society, London, 1962), p. 737.

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TABLE I. Sample listing, orientation, and room-temperature mobility, piezoresistance (π_ρ) and piezo-Hall effect (π_{Hall}). (The latter two properties were obtained using uniaxial compression.)

Designation ingot, slice, or other	Sample[a] code No.	Length orientation	μ_0 (cm^2 V^{-1} sec^{-1})	$-\pi_\rho$ (10^{-12} cm^2/dyn)	$-\pi_{\mathrm{Hall}}$ (10^{-12} cm^2/dyn)
Undoped					
No. 85	*B*-1.9-14	[110]	6120	100	101
N-8	*N*-8.4-14	[100]	4300	89	89
N-14	*N*-1.5-15	[100]	4990	70	71
G-97(260/274)	*M*-1.9-15	[100]	4910	67	66
G-97(260/274)	*M*-1.8-15	[110]	5250	69	64
14 *BHN*-Ca5	*I*-1.8-15	[100]	5250	17.6	15
14 *BHN*-Ca5	*I*-1.4-15	[110]	6280	20.7	20
	B(*T*)-2.6-15	[~211]	6750	18.0	24
*G*1112	*M*-2.8-15	?	4400	58	65
No. 91*A*	*B*-6.9-15	[110]	5250	19.3	
No. 107	*B*-9.3-15	[110]	5800	9.5	
No. 107	*B*-1.0-16	[100]	5730	8.3	6.0
No. 107	*B*-1.1-16	[110]	5560	8.3	6.9
No. 116	*B*-3.7-16	[110]	4520	4.2	
Vanadium doped					
*GC*238/10	*T*-9.3-12	?	350		
	T-1.9-13	?	3900		

[a] The letter in the sample code number indicates the source according to the following:

B-Bell and Howell Research Center
B(*T*)-Bell and Howell via Texas Instruments
I-IBM Research Center
M-Monsanto
N-Not certain (Probably *T*, see Ref. 9)
T-Texas Instruments

The numbers in the sample code number indicate the room-temperature carrier concentration: thus, 1.9-14 means 1.9×10^{14} cm^{-3}.

and of uniaxial compression at a number of temperatures, in addition to room temperature, on samples having a variety of low carrier concentrations.

In this paper our investigation will be described and most of the results presented and discussed. An analysis of some of the piezo-Hall results has been given in a previous paper.[11] The model used therein, which involved de-ionization of nonshallow donors due to pressure, will also be used herein to fit piezo-Hall data from 195 to 300°K on additional undoped samples not included in that paper. The nature of the nonshallow donor levels, whose presence is deduced from fitting the Hall data, will be discussed by comparing their pressure dependence with that of band states in GaAs and of nonshallow impurity levels in germanium and silicon, and with the results of some theories of impurity states. Further elucidation of these nonshallow donor levels will be provided by consideration of piezo-Hall and piezoresistivity data on vanadium-doped samples, of chemical impurities revealed by mass-spectrographic analysis, and of donor levels of similar energy due presumably to lattice defects.

Explanation of our piezo-Hall data at lower temperatures will be only qualitative and will involve a different, stress-dependent donor level than that involved at higher temperatures.

The variation of mobility of our undoped samples with pressure will be presented and compared with the pressure dependence of the effective electron mass. The influence of pressure-dependent screening on the mobility will also be considered.

II. EXPERIMENTAL DETAILS

The samples were cut by means of a diamond wheel from *n*-type GaAs obtained from a number of sources as indicated in Table I. Crystallographic orientations and some room-temperature characteristics of the samples are given in Table I also. The carrier concentration n_0 was deduced from the respective Hall coefficient at zero applied pressure, $R_H(P=0)$, measured with a field of 4500 G, by means of the relation $n_0=1/eR_H(P=0)$.

After being sawed, the samples were lapped and then etched for ~3 min with a solution of 1 HNO$_3$: 1 HCl: 2 H$_2$O. Platinum wires 0.002 in. in diam were soldered to the samples with Sn$_{0.97}$-Sb$_{0.03}$ alloy using ZnCl flux. In many instances the initial contacts were rectifying and of high resistance (100 kΩ or more). This was corrected by discharging a 0.5-μF condenser charged to $\lesssim$1500 V through the contacts a number of times, each time the polarity of the discharge being reversed. After this procedure, rectification had disappeared, and contact resistances were usually below 100 Ω, although for one sample they were as much as 2000 Ω.

Uniaxial stress was applied to samples mounted vertically in a holder via nylon end cups by means of a push tube inside of a larger tube which supported

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[11] R. J. Sladek, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris 1964* (Dunod Cie., Paris, 1964), p. 545.

the holder, both tubes being of type-304 stainless steel. Weights placed on a tray attached to the top end of the push tube provided the force. The sample holder and the lower parts of the push and support tubes were immersed in various baths held in an open Dewar flask.

Hydrostatic pressure was generated and measured by means of an apparatus assembled from commercial components.[12] The bomb itself was constructed of Be-Cu similar to designs for nonmagnetic pressure vessels in the literature[13] with the electrical leads being led out of the bomb by means of "Aeropak," which consists of a metal sheath tube inside of which are the wires insulated by tightly packed MgO.[14] The bomb was immersed in a bath of oil, freon, or dry ice and isopentane held in a Dewar flask. For the few measurements made above room temperature a tape-type electrical heater was used in the oil bath. Temperatures were measured with a copper-constantan thermocouple.

For the Hall measurements the magnetic field was provided by a 4-in. Varian magnet and measured with a Rawson rotating coil fluxmeter. To ensure that the magnetic field stayed constant, the current through the magnet was monitored potentiometrically.

Electrical quantities were measured by a dc system employing a potentiometer (*L* and *N* type *K*-3) and null detector (*L* and *N* microvoltmeter usually).

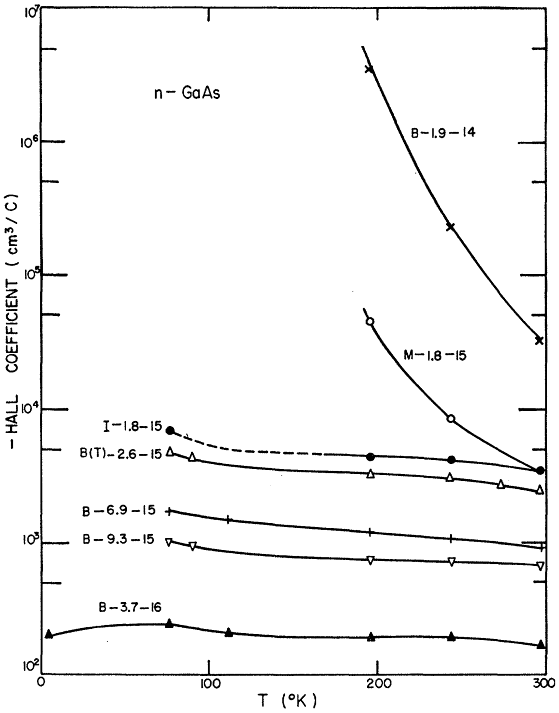

FIG. 1. Hall coefficient versus temperature of undoped, *n*-type GaAs samples.

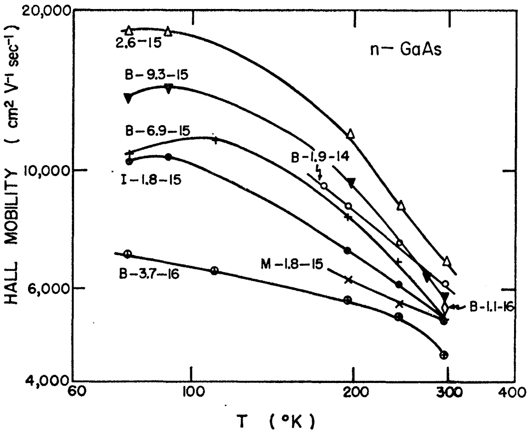

FIG. 2. Hall mobility versus temperature of undoped, *n*-type GaAs samples.

III. RESULTS AND DISCUSSION

The Hall coefficients and mobilities for various samples at atmospheric pressure are shown as a function of temperature in Figs. 1 and 2. The room-temperature values of the carrier concentration (taken as $1/R_He$) and the mobility for all of the samples used in this investigation are included in Table I.

From Fig. 1 it can be seen that the undoped samples fall into two groups: the Hall coefficients of samples of one group being strongly temperature-dependent and those of samples of the other group being only slightly temperature-dependent. The most common semiconducting *n*-type GaAs belongs to the latter group.

The mobility results given in Fig. 2 and Table I indicate that all of the samples, except the vanadium-doped one (T-9.3-12), must have quite small total concentrations of static scattering centers.

A. Uniaxial Compression

The quality of the uniaxial compression data and the sample arrangement is illustrated in Fig. 3 which shows the relative change of resistance voltage in zero magnetic field and the relative change of Hall voltage in a field of 4400 G as a function of the applied weight (and the stress deduced therefrom). Note in Fig. 3 the near equality in the relative changes of resistivity and of Hall effect. The incidence and significance of this occurrence will be discussed shortly.

Piezoresistance data were taken to check for a dependence on crystallographic orientation of the stress by using, when possible, two samples cut from the same slice of material but having lengths parallel to different crystallographic directions ([100] and [110]). The values of π_{11} and $\frac{1}{2}(\pi_{11}+\pi_{12}+\pi_{44})$ obtained thus for two pairs of sample, one pair from each $|dR_H/dT|$

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[12] American Instrument Company, Inc., Silver Spring, Maryland.

[13] W. Paul, G. B. Benedek, and D. M. Warschauer, Rev. Sci. Instr. **30**, 874 (1959).

[14] R. H. Cornish and A. L. Ruoff, Rev. Sci. Instr. **32**, 639 (1961).

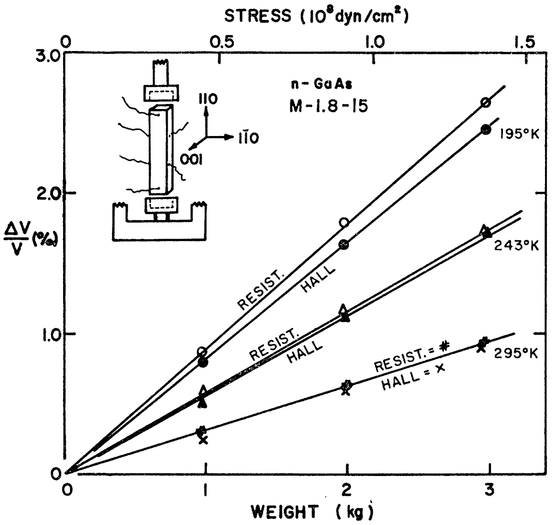

FIG. 3. Relative changes of resistance and Hall voltage versus weight used to provide uniaxial compression at three temperatures.

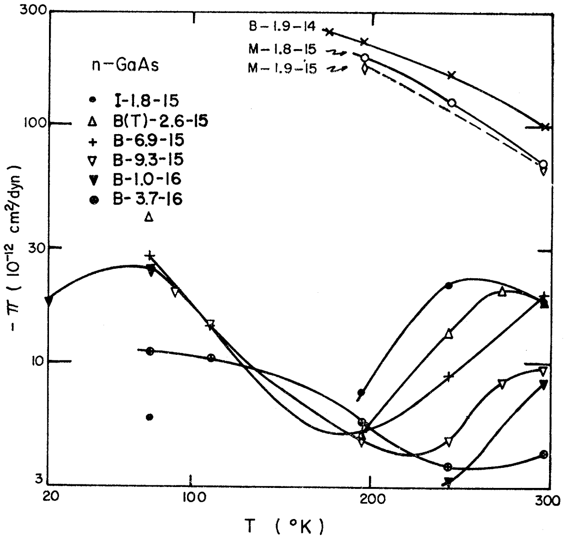

FIG. 4. Piezoresistance measured with uniaxial compression versus temperature of undoped, n-type GaAs samples.

group, are listed in Table II. From Table II it can be seen that the piezoresistance is independent of the crystallographic orientation of the stress. This independence of orientation is consistent with previous piezoresistance results[1,3] and indicates conduction in a single, nondegenerate band at $\mathbf{k}=0$ since anisotropic piezoresistance is characteristic of multivalley and degenerate bands. However, the magnitude of the piezoresistance at room temperature is greater than that measured previously[1,3] (which was on samples with higher carrier concentrations and/or lower mobilities) and is also greater than that expected for a band at $\mathbf{k}=0$ which is as far away from other bands as it seems to be in GaAs (about 1.4 eV from the valence band and 0.3 eV from the closest subsidiary minimum)[5] since the stresses in question are insufficient to cause transfer of carriers into even the closest of the other bands[5] or to cause interband scattering. (Evidence bearing on the latter will be presented in Sec. IIIB3.)

The piezoresistance of various samples is plotted as a function of temperature in Fig. 4. Note that two general types of behavior occur: very large piezoresistance which increases monotonically as the temperature is decreased, and smaller piezoresistance which exhibits a minimum below room temperature. Comparison with Fig. 1 reveals that the large monotonic piezoresistance occurs in just those samples exhibiting a strongly temperature-dependent Hall coefficient, and the smaller piezoresistance, which exhibits a minimum, occurs in samples exhibiting a weakly temperature-dependent Hall coefficient. In order to account for the piezoresistance properly, it is useful to have piezo-Hall data. Since the latter are more difficult to obtain, they are less complete and, when the effects get small, they are much less accurate than the piezoresistance data. However, the following qualitative picture emerges: The piezo-Hall effect is always independent of the crystallographic orientation of the sample. It is usually about equal to, or only slightly smaller in magnitude than, the piezoresistance. That these features are true

TABLE II. Piezoresistance of n-GaAs (units: 10^{-12} cm^2/dyn).

	Large $\lvert dR_H/dT\rvert$[a]		Small $\lvert dR_H/dT\rvert$[b]		Sample length orientation	Stress
	296°K	195°K	296°K	195°K		
Measured:						
π_{11}	−67	−179	−17.6	−7.5	[100]	Uniaxial
$\frac{1}{2}(\pi_{11}+\pi_{12}+\pi_{44})$	−69	−195	−20.7	−7.75	[110]	Uniaxial
$\pi_{11}+2\pi_{12}$	−205	−623	−55.4	−24.0	[110]	Hydrostatic
Deduced:						
π_{12}	−69	−222	−18.9	−8.2		
$\pi_{11}-\pi_{12}$	2	43	1.3	0.2		
π_{44}	−2	11	−4.9	0.7		

[a] Samples M-1.9-15 and M-1.8-15.
[b] Samples I-1.8-15 and I-1.4-15.

for room temperature can be seen by reference to Table I. Only when the piezoresistance has its minimum is it found that the piezo-Hall effect may be much smaller than the piezoresistance (about $\frac{1}{2}$ of the latter).

Thus, from the uniaxial compression data, it can be seen that in most instances the piezoresistance is due mainly to a reduction in the carrier concentration, as evidenced by the piezo-Hall effect. The reason for the change in carrier concentration above 195°K becomes quite clear from analysis of Hall effect versus hydrostatic pressure data at various temperatures as done in Ref. 11 and in the following section, namely: The ionization energy of nonshallow donors in the samples is increased by the pressure.

The reason for the Hall effect's having a different temperature and pressure dependence in one sample from that in another is the different relative concentrations of shallow donors and acceptors and of nonshallow donors. Thus, samples having more acceptors than shallow donors are *n*-type only because the nonshallow donors are available to contribute the conduction-band electrons. In this case the conduction electron concentration is very sensitive to, and a monotonic function of, pressure and temperature. However, samples in which the concentration of acceptors does not exceed the concentration of shallow donors derive their conduction electrons from both kinds of donors. As the temperature is decreased sufficiently, all the nonshallow donor levels become filled even in the absence of applied stress, the piezo-Hall effect disappears, and the piezoresistance becomes very small (the dependence of mobility on stress still causing some piezoresistance).

In order to understand the recovery of the piezoresistance at temperatures below that at which it had a minimum, we note that at such temperatures the piezo-Hall effect again becomes comparable in magnitude to the piezoresistance. Therefore, freezeout of carriers into a stress-dependent level again suggests itself. However, in this case, the piezo-Hall data are not complete, nor accurate enough, for a quantitative analysis which might lead to a deduction of the concentration and ionization energy of such levels. Other evidence for the presence of such levels may perhaps be provided by the slightly increased temperature dependence of the Hall effect between about 100 and 77°K (see Fig. 1).

B. Hydrostatic Pressure

1. Undoped Samples

Representative Hall effect and resistivity data are shown in Figs. 5 and 6. The ratio of the quantity at pressure P to that at zero applied pressure is plotted as a function of pressure. Note that a logarithmic scale is used for the ordinate in Fig. 5. Thus both the Hall effect and the resistivity of the sample shown in Fig. 5 increase almost exponentially with pressure at about the same rate, and the rate of increase is higher as the temperature becomes lower. This, of course, is as expected for the sample in question because of the strong temperature dependence of its Hall coefficient (see Fig. 1) and the behavior of the piezoresistance measured with uniaxial compression (see Fig. 3). In Fig. 6 on the other hand a linear scale is used for the ordinate. Thus we note that the pressure dependence of the Hall effect and the resistivity are quite small compared with those shown in Fig. 5. In addition, after increasing linearly with pressure at low pressures, the Hall effect begins to saturate at higher pressures while the resistivity keeps increasing, although in one case at a much smaller rate than at low pressures. Finally, from Fig. 6, it can be seen that the dependence of the Hall effect and of the resistivity on pressure both decrease with decreasing temperature. All of these effects are consistent with the weak temperature dependence of Hall coefficient and the behavior of the piezoresistance and piezo-Hall effect measured using uniaxial compression.

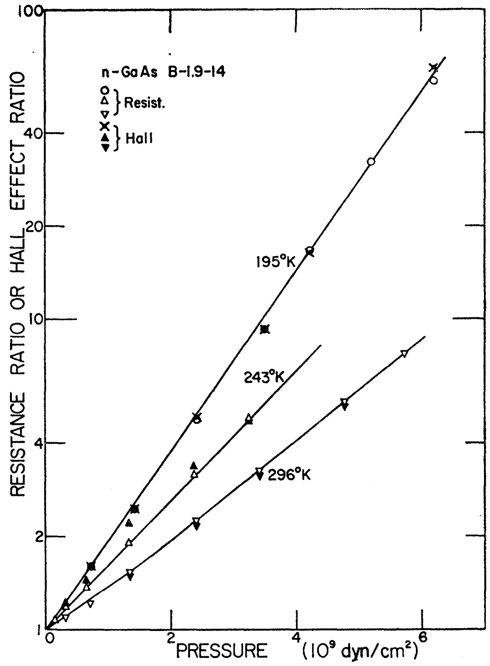

FIG. 5. Ratios of resistance and Hall effect to the respective zero-pressure values versus hydrostatic pressure at three temperatures.

Numerical values of the piezoresistance at low hydrostatic pressure, i.e., $\pi_{11}+2\pi_{12}$, for two samples are included in Table II. Combining these values with those obtained using uniaxial compression we obtained the values of π_{12} and of the shear coefficients, $\pi_{11}-\pi_{12}$, and π_{44}. They are also given in Table II. The smallness of both the shear coefficients compared with π_{11} or π_{12} is consistent only with conduction in a nondegenerate band at $\mathbf{k}=0$.

a. Model for the Hall effect. As in Ref. 11, the concentration of carriers in the conduction band n is

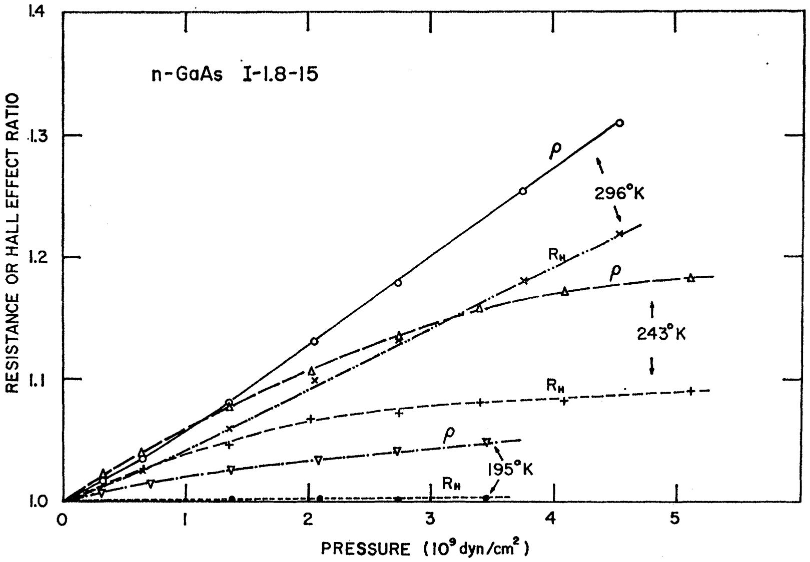

FIG. 6. Ratios of resistivity and Hall effect to the respective zero-pressure values versus hydrostatic pressure at three temperatures.

attributed to the combined effects of shallow donors of concentration N_D, acceptors of concentration N_A, and nonshallow donors of concentration N_d, with the ionization energy $-E_d$ of the latter increasing linearly with applied pressure, i.e., $E_d = E_{d0} + (\Delta E_d/\Delta P)P$. When the shallow donors are all ionized regardless of applied pressure and temperature and the conduction electrons obey nondegenerate statistics, then

$$n = N_D - N_A + N_d/[1+(ng/N_c)\exp\{-E_d/kT\}], \quad (1)$$

where g is the statistical degeneracy of the nonshallow donor level and $N_c = 2(2\pi m^* kT/h^2)^{3/2}$, with the symbols in the latter having their usual meanings. We shall take $n = 1/|R_H|e$ and use $g=2$ and $m^* = 0.072\ m_0$ as in Ref. 11.

b. Fitting the Hall effect data. In Ref. 11 Eq. (1) was found to fit Hall effect-versus-pressure data and to account for the zero-pressure carrier concentrations at various temperatures remarkably well. The fitting of those data will not be shown here. Instead, in Figs. 7 and 8 are shown data and curves calculated using Eq. (1) for two samples not treated in Ref. 11. The values of the parameters used for fitting the data on these samples are given in Table III. For use in later sections the results for the samples of Ref. 11 are also included in Table III.

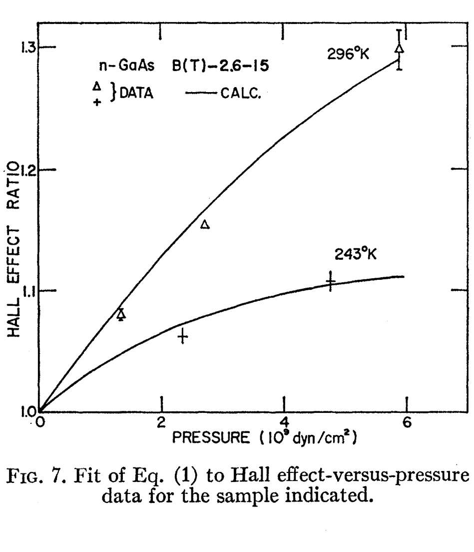

FIG. 7. Fit of Eq. (1) to Hall effect-versus-pressure data for the sample indicated.

c. Discussion. From Table III it can be seen that the values of $-E_{d0}$ for four of the samples are very nearly equal and that the value of $-E_{d0}$ for *B*-1.9-14 is only slightly higher than for the others. All the values of $|E_{d0}|$ are much greater than the hydrogen-like impurity value of ~0.006 eV. These facts coupled with the fact that $-\Delta E_d/\Delta P$ has about the same value in all samples suggest the presence of one and the same type of nonshallow donor in all the samples. Note that both of the new samples and one of those reported on in Ref. 11 have values of $N_A - N_D < 0$. All three of these samples are characterized by Hall coefficients which are only weakly dependent on temperature and pressure. (See Figs. 1, 7, and 8 and Ref. 11.)

TABLE III. Level information deduced from electrical measurements.

Sample	$-E_{d0}$ (eV)	$-\Delta E_d/\Delta P$ (10^{-12} eV cm²/dyn)	N_d	$N_A - N_D$
			(10^{15} cm^{-3})	
B-1.9-14[a]	0.203	10.2	4.6	1.3
M-1.8-15[a]	0.175	10.0	26	0.70
I-1.8-15[a]	0.164	8.85	2.5	−1.38
B(*T*)-2.6-15	0.168	9.5	7.0	−1.86
B-1.1-16	0.168	10.0	17.5	−10.50

[a] Reported on in Ref. 11.

In contrast are the other two samples which have values of $N_A - N_D > 0$ and are characterized by Hall coefficients having a very strong temperature dependence and an exponential-like pressure dependence. (See Figs. 1 and 5 and Ref. 11.) The excess of acceptors over shallow donors means that these samples would be p type in the absence of nonshallow donors so that the latter determine the concentration of conduction electrons. The great sensitivity of the conduction electron concentration to temperature in these samples then results of course from the fact that $|E_{d0}| \gg kT$. The strong pressure dependence of the carrier concentration and the lack of saturation of the Hall effect in these samples are also explainable by all the carriers being derived from nonshallow donors with pressure-dependent ionization energy.

The values of $-\Delta E_d/\Delta P$ for all the samples are very close to those obtained from the pressure dependence of the gap between the (lowest) conduction band and the valence band (9.5×10^{-12} eV cm^2/dyn and 12×10^{-12} eV cm^2/dyn)[2] and deserve some comment. First of all, such a correspondence between the pressure dependence of donor ionization energy and the energy gap has been found for nonshallow donor levels due to gold in germanium and silicon. However, unlike our nonshallow donor levels, the gold donor levels are nearer to the valence band than to the conduction band. In addition gold also gives rise to acceptor levels in Ge and Si. Thus, it might be argued that the gold donor state is connected with valence-band states. In contrast, our nonshallow donor level is quite close to the $\mathbf{k}=0$ conduction band ($\sim$0.2 eV) and is also closer to the subsidiary conduction-band minimum ($E_{\text{sub}} - E_{\mathbf{k}=0\ \text{band}} + |E_d| \approx 0.5$ eV at $P=0$) than it is to the valence band ($E_{\text{gap}} - |E_d| \approx 1.2$ eV at $P=0$). Also, it should be noted that the subsidiary conduction-band minimum in GaAs moves down relative to the $\mathbf{k}=0$ band at about the same rate as we have found that $|E_d|$ increases with pressure. Since it has been found that deeper levels in GaAs have smaller pressure dependences[15] than does our nonshallow donor level, Paul has suggested that perhaps our level is derived more from the subsidiary minimum than from the minimum at $\mathbf{k}=0$.[16] If this is the case, the question of how to construct a wave function and account for the location of our nonshallow level remains, since theory[17,18] indicates that localized states derived from subsidiary minima would have short lifetimes and be close in energy to the minima they are derived from.

Another theory[19] has tried to account for nonshallow impurity states in Ge and Si by assuming that the impurities causing them are interstitials and hence have potentials whose unshielded core parts are important enough to make nonshallow levels occur for some kinds of impurities. Indeed, the chemical impurities, which we deduce are the most likely providers of our nonshallow levels (see Sec. IIIC), could very well be interstitials from rough size considerations. Unfortunately, this theory does not seem to us to be able to account for the pressure dependence of the ionization energy of our nonshallow levels, even in a qualitative manner.

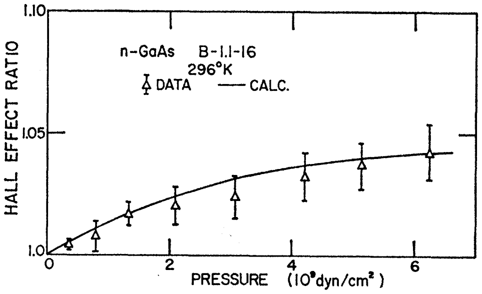

FIG. 8. Fit of Eq. (1) to Hall effect-versus-pressure data for the sample indicated.

2. *Vanadium-Doped Samples*

In an effort to learn more about the nature of our nonshallow donors, measurements were made of the effect of hydrostatic pressure on the resistivity of two vanadium-doped samples and on the Hall effect of one of these samples. Vanadium-doped samples were used because work by Haisty seemed to indicate that vanadium impurity gave rise to a donor level about 0.2 eV below the conduction band.[20] We found that the resistivity of both V-doped samples increased exponentially with pressure. Figure 9 shows data for one of the samples. The pressure dependence of the Hall coefficient at each temperature yields very nearly the same value for $-\Delta E_d/\Delta P$, namely, 10×10^{-12} eV cm^2/dyn. The magnitudes of the Hall coefficient at zero applied pressure for the two temperatures shown yield a value for $-E_{d0}$ of 0.15 eV and for $\{[N_d/(N_A - N_D)] - 1\}$ of 0.16. It was not possible to obtain values of N_d and $N_A - N_D$ separately because the carrier concentration is apparently very small compared with $|N_D - N_A|$, in which case Eq. (1) reduces to

$$n \approx (N_c/g)\{[N_d/(N_A - N_D)] - 1\} \exp(E_d/kT).$$

Although the value of $-E_{d0}$ is somewhat smaller than that obtained for most of our undoped samples, we believe that it corresponds to the same kind of nonshallow donor level as occurs in the latter for two reasons: First, our analysis of more detailed, zero-pressure Hall data taken down to lower temperatures by Haisty on a sample from the same vanadium-doped crystal yields a value of $-E_{d0} \approx 0.17$ eV which is of

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[15] J. Feinleib, S. Groves, W. Paul, and R. Zallen, Phys. Rev. **131**, 2070 (1963).

[16] W. Paul (private communication); Ref. 11 discussion.

[17] H. Kaplan, J. Phys. Chem. Solids **24**, 1593 (1963).

[18] G. A. Peterson, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris 1964* (Dunod Cie., Paris, 1964), p. 771.

[19] P. E. Kaus, Phys. Rev. **109**, 1944 (1958).

[20] R. W. Haisty (private communication).

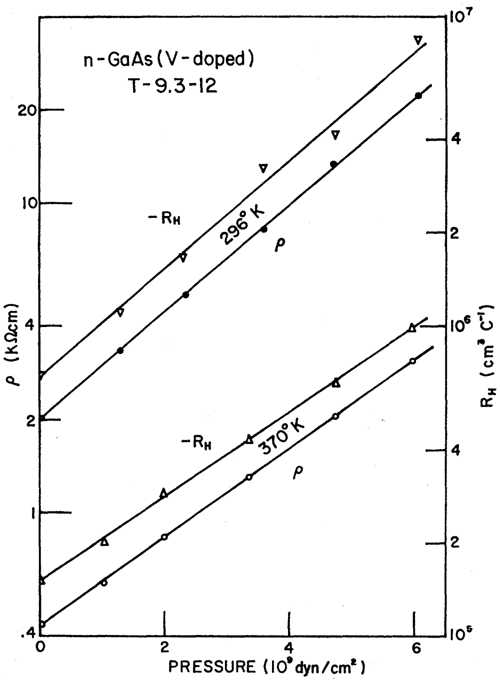

FIG. 9. Hall effect and resistivity-versus-pressure data for vanadium-doped, n-type GaAs.

course just what we obtained for most of our undoped samples. Second, the value we obtained for $-\Delta E_d/\Delta P$ for the V-doped sample is equal, within experimental uncertainty, to that obtained for our undoped samples. Further discussion of the possible nature of our non-shallow donors will be given in Sec. IIIC.

3. Mobility

The dependence of the mobility on pressure was deduced from our Hall effect and resistivity-versus-pressure data on various undoped samples. In all cases it was found that the mobility decreased linearly with increasing pressure. A summary of the rates of change of mobility with pressure for various samples and temperatures is given in Table IV. From Table IV we see that the values of $-\Delta\mu/\Delta P$ are comparable to, or less than, the rate of increase of gap with pressure except in the case of sample M-1.8-15. This suggests that, except in the case of M-1.8-15, the variation of the mobility with pressure is due to the pressure dependence of the effective mass, since the latter is related to the energy gap through the f-sum rule.[21] If we assume that the mobility is proportional to $(m^*)^{-r}$, and m^* is proportional to the energy gap, we obtain values of r at 296°K ranging between 0.2 and 2.0 for all samples except M-1.8-15. Although such a wide range of values of r is rather surprising, some variation of r from sample to sample is to be expected since the dependence of mobility on mass depends on the kinds of scattering which are important. Thus, for example, disregarding screening effects, according to theory r should be equal to $\frac{3}{2}$ when polar optical mode scattering is predominant[5] and equal to $\frac{1}{2}$ when ionized impurity scattering[22] is predominant. The values we find for r do vary inversely with the magnitude of the room-temperature mobility at zero pressure and thus presumably the amount of nonlattice scattering. The pressure dependence of the mobility of sample M-1.8-15 seems to be too great to attribute to variation of m^* with pressure. Since the carrier concentration of this sample is reduced drastically by pressure, the mobility behavior could be explained by there being a large amount of nonlattice scattering present which is very sensitive to the amount of screening by charge carriers, for example, scattering due to space-charge regions[23] arising from an inhomogeneous distribution of impurities.[24] Such scattering, however, must not be important in the other undoped sample which exhibits a large decrease in carrier concentration with pressure (B-1.9-14) since its mobility is only weakly pressure-dependent. Other evidence that the type of nonlattice scattering is different in M-1.8-15 from that in the other samples may be provided by the fact that the temperature dependence of the mobility of M-1.8-15 is less than that of the other undoped samples. (See Fig. 2.)

TABLE IV. Pressure coefficient of the mobility of undoped, n-type GaAs.

	$-(\Delta\mu/\Delta P)$ $(10^{-12}$ cm^2/dyn)	
Sample	296°K	195°K
B-1.9-14	9.8	1.5
M-1.8-15	34.5	34.5
I-1.8-15	15.5	15.5
$B(T)$-216-15	1.5	5.5[a]
B-1.1-16	13	

[a] At 243°K.

That the linear pressure dependence of the mobility can be accounted for as above indicates the absence of another mechanism sometimes responsible for mobility being pressure-dependent, namely, interband scattering.[25] Such scattering occurs when a subsidiary band is close enough to the primary one. Furthermore, such scattering is pressure-dependent if relative motion of the bands is caused by the pressure. An example is provided by n-type germanium in which case the rate of change of mobility with pressure is not constant with pressure (but becomes more negative as the pressure increases).[25] Since, for n-type GaAs, the sub-

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[21] See, e.g., R. W. Keyes, in *Solid State Physics Vol. 11,* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), p. 149.

[22] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950); H. Brooks, in *Advances in Electronics and Electron Physics,* edited by L. Marton (Academic Press Inc., New York, 1955), Vol. VII, p. 87.

[23] B. R. Gossick, J. Appl. Phys. **30**, 1214 (1959).

[24] L. R. Weisberg, J. Appl. Phys. **33**, 1817 (1962).

[25] M. I. Nathan, W. Paul, and H. Brooks, Phys. Rev. **124**, 391 (1961).

sidiary minimum is known to approach the primary one, the apparent absence of interband scattering implies that the subsidiary minimum is not very close to the primary one, which is in agreement with most other evidence.[26]

C. Impurities

The nature of the nonshallow donor levels has already been discussed in terms of derivation from band states and theories of impurity states. It remains to be seen if the nonshallow donor levels can be related to chemical impurities or other imperfections.

Chemical impurities will be considered first. We proceed by presenting in Table V some pertinent results of commercial mass-spectrographic analyses made on four of the materials from which the samples for our electrical measurements were obtained. In three of the cases the samples analyzed were cut from the same slice as were the samples used for the electrical measurements. In the fourth case (No. 85), the samples analyzed were from the same ingot but not from the same slice as the sample (*B*-1.9-14) used for electrical measurements.

In Table V ordinary shallow donors[27] are grouped together in the first row while acceptors are grouped into rows 2, 3, and 4. The acceptors in row 2 give shallow levels[27] and are the most often used *p*-type dopants. The acceptors in row 3 give deeper acceptor levels, and have smaller segregation coefficients than those in row 2.[28] Vanadium is put by itself in row 4 because we have classified it as an acceptor although Haisty[20] has designated it a nonshallow donor. The reason for our classification is that, from consideration of the concentrations of impurities known to be donors or acceptors, the condition $N_A > N_D$ cannot be fulfilled in sample *T*-9.3-12 unless either V acts an acceptor, or else one, or both, of the undeterminable impurities sodium and tantalum are present in the correct amount and act as acceptors. Actually, sodium has been found to be an acceptor.[27] The necessity that the condition $N_A > N_D$ be fulfilled in sample *T*-9.3-12 is, or course, implied by the large, exponential-like dependence of the Hall coefficient on temperature and pressure which it exhibits as discussed previously. It might be noted that for two of the materials which provided our undoped samples the relationship between N_A and N_D is not quite the same as deduced from the electrical measurements. However the discrepancy is not nearly as large as it would be for the V-doped material if V (or some other acceptor) were not present in the latter.

TABLE V. Significant[a] impurity concentrations in atomic parts per million from mass-spectrographic analyses.[b]

Element(s) \ Material	#107	*G*-97(260/274)	#85	*GC* 238/10
Si+Se+S	0.37	0.55 (or 1.45)	0.14	0.44
Cd+Zn	0.3	0.6	0.1	0.10
Ni+Fe+Cr	0.12	0.40	0.04	0.02
V	...	...	...	1.6
H	0.88	0.35	0.11	0.41
C	0.51	1.4	0.08	0.34
N	0.28	0.42	0.07	0.50
O	5.0	54–0.66	0.64–3.2	2.8
F	0.05	0.35	...	0.006
K	0.1	0.07	0.02	0.15

[a] Not listed are (1) impurities having concentrations less than 0.03 ppm, (2) Al and Sb because presumably they are electrically neutral, (3) Ta because Ta slits are used in the spectrograph, and (4) Na because it is covered by $^{69}Ga^{+3}$.

[b] Made by Bell and Howell Research Center.

Now, to see if the nonshallow donors can be attributed to any of the other impurities listed in Table V, we shall compare the values of N_d (deduced from the electrical measurements) with the concentrations of these impurities. Converted into parts per million the values of N_d are as follows:

Sample	N_d
B-1.9-14	0.10 atomic ppm
M-1.8-15	0.60
B-1.1-16	0.40

Referring now to Table V we see that none of the "other" impurities were detected in exactly these concentrations. However, three of the impurities, namely, carbon, nitrogen, and oxygen, were detected in concentrations following the same relative trend as the values of N_d. Furthermore, nitrogen was detected in the same concentration ratios as found for N_d, namely, 1:6:4. Before concluding from this that nitrogen does indeed provide our nonshallow donors, a number of caveats must be mentioned. First, determination of the nitrogen content in the samples might be inaccurate because the samples were etched with HNO_3 (and HF) before analyses. Second, the absolute concentration of nitrogen detected is less than the respective values of N_d. Third, nitrogen has been found to be electrically neutral in GaAs.[27] However, this conclusion is probably based on there being no appreciable change of carrier concentration with nitrogen doping, and no such change need have occurred even if nitrogen provided a nonshallow level if enough shallow donors were present.

It should be noted that carbon and oxygen are detected in greater concentrations than is nitrogen, and they seem to act as donors,[29] the ionization energy of carbon being unknown, and that of oxygen being large, 0.7 eV.[30,31] Although the latter level is much

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[26] For a summary of this evidence see Ref. 5.

[27] L. R. Weisberg, F. D. Rosi, and P. G. Herkart, in *Properties of Elemental and Compound Semiconductors*, edited by H. C. Gatos (Interscience Publishers, Inc., New York, 1960), p. 25.

[28] R. W. Haisty and G. R. Cronin, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris 1964* (Dunod Cie., Paris, 1964), p. 1161.

[29] Carbon is specified as the dopant in some *n*-type GaAs listed in Material Inventories of Bell and Howell Research Center, and oxygen has been found to be a deep donor by various authors (see Refs. 30 and 31).

[30] R. W. Haisty, E. W. Mehal, and R. Stratton, J. Phys. Chem. Solids **23**, 829 (1962).

[31] J. F. Woods and N. G. Ainslie, J. Appl. Phys. **34**, 1469 (1963).

deeper than our nonshallow level, the possibility remains that oxygen might also provide another level of suitable depth. In view of the above considerations we believe that neither nitrogen, nor carbon, nor oxygen, should be ruled out as possible sources of our nonshallow donor levels.

D. Lattice Defects

Since other investigators[32] have found donor levels near 0.2 eV in GaAs due to one member of a pair of lattice vacancies (the other member of the pair providing acceptor levels about 0.2 eV above the valence band), it is germane to consider whether our nonshallow donor levels might be of similar origin. In order to do so, we note that the paired vacancies were electrically active in sufficient concentrations only after special annealing treatments under conditions which depended on how the GaAs had been grown from the melt. Annealing in copper produced "traps" (including the 0.2-eV levels) both in horizontal Bridgman and floating zone material, while annealing without copper produced traps only in floating zone material. In all cases the material was of high resistivity ($>10^7$ Ω-cm at 300°K).

In contrast, our samples are of materials whose preparation did not involve the above factors which seem to be needed to produce defect levels. Specifically, no special annealing was done, growth was by the Czochralski or horizontal Bridgman methods, and no copper was detected in the four of our sample materials which were analyzed. Also, our samples were of low resistivity. Thus, we do not think it likely that lattice defects are responsible for our nonshallow donor levels.

It is interesting to note that Blanc *et al.*[32] indicate that their samples typically had concentrations of *carbon* and *oxygen* of about 5 atomic ppm. This raises the question of whether perhaps carbon and/or oxygen are involved in the formation of some of their traps.

IV. CONCLUSIONS

Conduction in *n*-type GaAs of relatively low carrier concentrations (but not of the so called high resistivity variety) is due to electrons in a band at $\mathbf{k}=0$. Dependence of the electrical properties on stress is due to both the carrier concentration and mobility being stress-dependent. The stress dependence of the carrier concentration arises from the presence of nonshallow donor levels having stress-dependent ionization energies and that of the mobility arises mainly from the effective mass being stress-dependent.

The 0.17-eV nonshallow donor level we observe seems very likely to be due to carbon, nitrogen, or oxygen impurities rather than to vanadium impurity or lattice defects.

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[32] J. Blanc, R. H. Bube, and L. R. Weisberg, J. Phys. Chem. Solids **25**, 225 (1964).