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Effect of Te and S Donor Levels on the Properties of $GaAs_{1-x}P_x$ near the Direct-Indirect Transition*

M. G. CRAFORD,† G. E. STILLMAN,‡ J. A. ROSSI, AND N. HOLONYAK, JR.
Department of Electrical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois

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The effect of donor impurity levels associated with higher-lying conduction-band minima on the direct–indirect transition in heavily doped $GaAs_{1-x}P_x$ has been studied. Hall-coefficient measurements from 55 to 400°K and resistivity measurements under hydrostatic pressure between 0 and 7 kbar at 300, 195, and 77°K have been made throughout the alloy composition range. The behavior of Te-doped crystals can best be explained by an impurity level ~0.03 eV below and associated with the [100] minima. The pressure coefficient of this level with respect to the [000] minimum is about 10.5×10^{-3} eV/kbar. Two impurity levels are found in S-doped crystals. The deeper of these two levels is ~0.04 eV beneath the [000] minimum for crystal composition $x=0.30$; the depth increases to ~0.21 eV at $x=0.45$. For further increase in x, this level becomes shallower. A persistent photoconductive effect is exhibited by this level at $T\leq100$°K. This behavior has been studied throughout the alloy composition range by means of photo-Hall measurements. The pressure coefficient of the deeper S level with respect to the [000] minimum is $(10.8\pm0.3)\times10^{-3}$ eV/kbar. From this and from the effect of crystal composition on the dependence of resistivity on pressure, it is concluded that the deeper S level is associated with the [100] conduction-band minima. At 77°K a second S level is observed which at $x=0.30$ is degenerate with the [000] minimum and has an estimated depth of 0.06 eV beneath the [100] minima. This level has a pressure coefficient of $(10.0\pm0.4)\times10^{-3}$ eV/kbar with respect to the [000] minimum, and is observed at 77°K because of the inability of the deeper S level to accept additional electrons when $T\leq100$°K. The mobility ratio of the two bands, $\mu(000)/\mu(100)$, is 15–30 at 300 and 195°K but increases to 60–100 at 77°K. The phosphorus concentration x at which the [000] and [100] minima are equal in energy is $x=0.43\pm0.01$ at 77°K and 0.45 ± 0.01 at 300°K, implying that the separation between the minima increases with temperature at the rate of $\sim6\times10^{-5}$ eV/°K.

1. INTRODUCTION

SINCE 1962, when Holonyak and Bevacqua[1] announced the first p-n junction laser in the visible part of the spectrum in $GaAs_{1-x}P_x$, a considerable amount of work has been done in determining the physical properties of this material. Following the work of Ehrenreich,[2] it is now generally accepted that the band structure of $GaAs_{1-x}P_x$ consists essentially of a high-mobility, low-effective-mass minimum at [000] in the Brillouin zone and six equivalent low-mobility, high-effective-mass minima in the [100] directions. A schematic diagram of the band structure of $GaAs_{1-x}P_x$ is shown in Fig. 1. As GaP is added to the GaAs system, the GaAs band edges (solid lines) sweep continuously through the ruled areas and approach the GaP band edges (dashed lines). Essentially this same variation occurs when the alloy composition is maintained constant and hydrostatic pressure is applied. An increase in hydrostatic pressure of 0.7 kbar is approximately equivalent to a 1.0% increase in alloy composition.

The effective mass of the Γ minimum in GaAs is about $0.072m_0$ for the doping concentration of interest here,[3] and the effective mass increases linearly with alloy composition roughly as $m^*=0.072m_0(1+x)$.[4] The density-of-states effective mass of the [100] minima is $1.2m_0$, which is in good agreement with that measured by Faraday rotation if six equivalent minima are assumed. This density-of-states effective mass is assumed to be independent of composition and pressure. The mobility of electrons in the [000] minimum is essentially the same as that of GaAs; the mobility of carriers (electrons) in the [100] minima is much lower and is characteristic of GaP. For undoped material the ratio of the mobility of electrons in the Γ minimum to that of electrons in the [100] minima is quite large, with $b=\mu_1/\mu_2\approx30$ at room temperature. The mobility ratio decreases somewhat for heavily doped crystals.

Because of the large density of states and low mobility of the indirect [100] minima, a sizeable change in the bulk properties of the material is expected as x approaches 0.45. One such change which occurs in a small composition range is the decrease in the mobility from a value characteristic of GaAs to a value characteristic of GaP.[5] Another rather abrupt change occurring in a small composition interval is the threshold current density (and efficiency) of p-n junction lasers. Studies of $GaAs_{1-x}P_x$ laser diodes indicate that the threshold current densities at 77°K remain quite low

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† Present address: Central Research Department, Monsanto, St. Louis, Mo.

‡ Present address: Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Mass.

[1] N. Holonyak, Jr., and S. F. Bevacqua, Appl. Phys. Letters **1**, 82 (1962).

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

[3] H. Piller, in *Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, 1966* (Physical Society of Japan, Tokyo, 1966).

[4] D. E. Hill, Bull. Am. Phys. Soc. **11**, 205 (1966); **12**, 657 (1967).

[5] J. J. Tietjen and L. R. Weisberg, Appl. Phys. Letters **7**, 261 (1965).

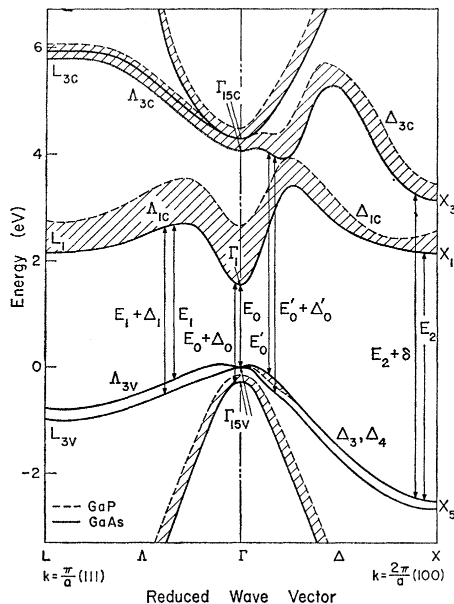

FIG. 1. Energy-band structure of the $GaAs_{1-x}P_x$ alloy system, obtained by superimposing the energy-band models for GaAs and GaP. As GaP is added to GaAs, the GaAs band edges (solid lines) sweep through the ruled areas and approach the GaP band edges (dashed lines). Increasing pressure has the same effect as increasing GaP concentration x (cf. Figs. 15 and 16).

at values around 3 000 A/cm^2 for compositions out to $x=0.33$. Beyond this composition the threshold current densities increase drastically.[6] The highest composition at which lasing action has been reported is $x=0.405$.[7] At values of x significantly less than that of the direct-indirect transition, the transfer of electrons to the indirect minima is expected to cause an increase in threshold current density and a decrease in recombination radiation efficiency. However, the magnitude of the decrease in efficiency at 77°K cannot be explained simply on the basis of the transfer of electrons to the indirect valleys.[8] One cause of this additional decrease in efficiency is the transfer of electrons from the direct minimum to shallow donor levels associated with the [100] minima.[9] Previously, experimental evidence has been obtained for impurity levels associated with subsidiary conduction-band minima by mobility measurements in GaSb [10] and from pressure measurements on GaAs,[11] GaSb,[12,13] and CdTe,[14] as well as from the behavior of certain $GaAs_{1-x}P_x$ laser diodes.[9] These levels have been studied theoretically by several authors,[15–17] but these theoretical results apply only to impurity levels which are close in energy to the band minima with which they are associated.

In this paper, we present electrical and pressure measurements on Ga(AsP) which further elucidate the direct-indirect transition and which describe the position of Te and S donor levels near subsidiary band minima.

2. EXPERIMENTAL

The $GaAs_{1-x}P_x$ crystals used in this work were prepared by a closed-tube halide-vapor-transport process which has been described in detail previously.[18] The compositions of most of the crystals studied have been checked by x-ray-diffraction patterns of powdered samples with a silicon reference. Hall-effect and pressure measurements were made on single-crystal cloverleaf samples of two sizes, either $\frac{1}{8}$ or $\frac{3}{8}$ in. in diam. After lapping and etching of the samples, small alloy contacts were applied in a hydrogen atmosphere. Measurements made both before and after etching gave identical results. For low-resistivity samples in the GaAs-rich composition range, indium contacts were satisfactory at all temperatures. However, for high-resistivity samples of larger GaP concentrations, it was found that an In-Pb-Te alloy gave better ohmic contacts at low temperatures.

The Hall and resistivity measurements which were made were interpreted according to the van der Pauw analysis.[19] The Hall coefficients were measured in a magnetic field of 6 kG, and both Hall and resistivity measurements were made with two different permutations of the sample contacts. When the magnetic field and current were reversed to eliminate the effect of thermal emf's, the readings with the two different permutations always agreed within the experimental precision of a few percent. This gives an indication of the macroscopic homogeneity of the crystals, which was previously known to be very good.[6]

The sample temperature was measured by a copper-constantan thermocouple close to the sample and was calibrated at liquid-nitrogen and ice temperatures. A small lightbulb was incorporated in the sample chamber so that measurements could be made both with the sample in the dark and illuminated.

The apparatus used for pressure measurements was

[6] C. J. Nuese, G. E. Stillman, M. D. Sirkis, and N. Holonyak, Jr., Solid State Electron. **9**, 735 (1966).
[7] J. I. Pankove, H. Nelson, J. J. Tietjen, I. J. Hegyi, and H. P. Maruska, Solid State Device Research Conference, Santa Barbara, Calif., June 1967 (unpublished). Also, RCA Review **28**, 560 (1967).
[8] H. P. Maruska and J. I. Pankove, Solid State Electron. **10**, 917 (1967).
[9] N. Holonyak, Jr., C. J. Nuese, M. D. Sirkis, and G. E. Stillman, Appl. Phys. Letters **8**, 83 (1966).
[10] R. T. Bate, J. Appl. Phys. **33**, 26 (1962).
[11] A. R. Hutson, A. Jayaraman, and A. S. Coriell, Phys. Rev. **155**, 786 (1967).
[12] B. B. Kosicki and W. Paul, Phys. Rev. Letters **17**, 246 (1966).
[13] B. B. Kosicki, W. Paul, A. J. Strauss, and G. W. Iseler, Phys. Rev. Letters **17**, 1175 (1966).
[14] A. G. Foyt, R. E. Halstead, and W. Paul, Phys. Rev. Letters **16**, 55 (1966).
[15] H. Kaplan, J. Phys. Chem. Solids **24**, 1593 (1963).
[16] G. A. Peterson, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 771.
[17] T. Shimizu, Phys. Letters **15**, 297 (1965).
[18] N. Holonyak, Jr., D. C. Jillson, and S. F. Bevacqua, in *Metallurgy of Semiconductor Materials*, edited by J. B. Schroeder (Interscience Publishers, Inc., New York, 1961), p. 49; C. M. Wolfe, C. J. Nuese, and N. Holonyak, Jr., J. Appl. Phys. **36**, 3790 (1965); C. J. Nuese, G. E. Stillman, M. D. Sirkis, and N. Holonyak, Jr., Solid State Electron. **9**, 735 (1966).
[19] L. J. van der Pauw, Philips Res. Rept. **13**, 1 (1958).

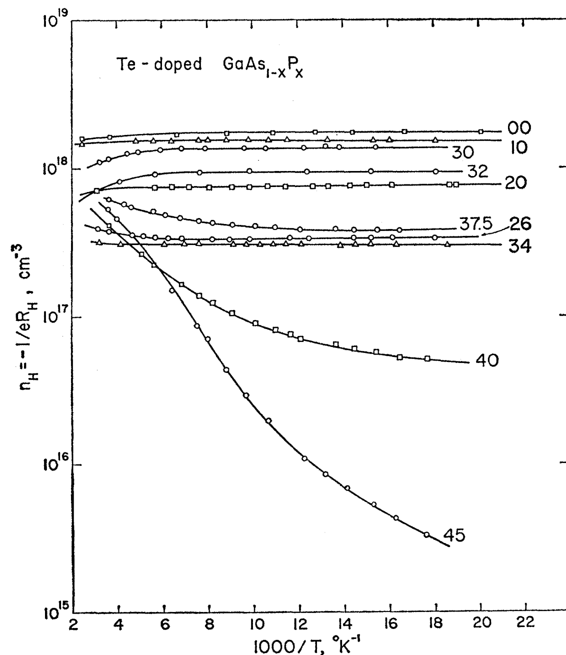

FIG. 2. Temperature dependence of Hall carrier concentration ($-1/eR_H$) for Te-doped $GaAs_{1-x}P_x$ crystals with direct band gap. (The sample designation, for example, 30 Te, indicates the mole percent of GaP in the crystal.)

essentially the same as that described by Fitchen.[20] The pressure medium was argon for 300 and 195°K experiments, and helium for 77°K experiments. The pressure vessels were supported in covered Dewars which contained baths of water, dry ice, and alcohol, or liquid nitrogen. The vessels were of conventional design[21] and had unsupported area seals with brass-indium-copper packings. The electrical leads to the samples were brought out by means of frozen oil seals.

3. Te-DOPED $GaAs_{1-x}P_x$ CRYSTALS

The results of Hall-effect measurements on some Te-doped samples are shown in Fig. 2. The carrier concentrations calculated from $n_H=-1/eR_H$ are essentially constant for samples 00Te and 10Te. This is expected since these samples are doped so heavily that there is no ionization energy of the Te donors and since the maximum in the two-band Hall constant or the minimum in n_H occurs at high temperatures for samples in this composition range. Sample 20Te shows a small increase in n_H as initially the temperature decreases; samples 30Te and 32Te show larger increases, increasing in that order. This is consistent with the two-conduction-band model which predicts that the minimum in n_H shifts towards lower temperatures as the mole fraction of GaP increases. The two-band model predicts that the minimum in n_H should continue to shift toward lower temperatures until $x=0.43$, but this is not observed experimentally. The Hall carrier concentration for sample 34Te is practically independent of temperature, while for samples 37.5Te and 26Te it decreases with decreasing temperature. For higher values of x the decrease in n_H as the temperature is lowered becomes larger, reaching a maximum at $x=0.45$. With further increase in x the curves become similar to those of heavily doped GaP with impurity banding.

It is possible that the disagreement in the shift in the minimum of n_H predicted by the two-band model from that observed experimentally can be explained by the variation of ΔE and b with temperature.[22] However, this does not seem probable since it would require that these parameters vary appreciably with crystal composition. A more likely explanation is that the Hall constant is influenced by an impurity band associated with the [100] minima, with a small contribution by a few deep levels.

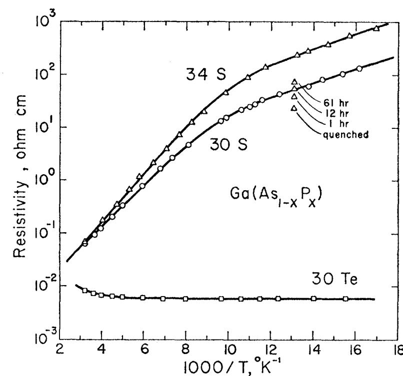

FIG. 3. Temperature dependence of resistivity for typical S-doped $GaAs_{1-x}P_x$ crystals. The data points at $1000/T=13$ were taken after the sample was rapidly cooled to liquid-nitrogen temperatures in the dark.

4. S-DOPED $GaAs_{1-x}P_x$ CRYSTALS

Behavior of Typical S-Doped Crystals

The dark-resistivity data for two S-doped samples of composition $x=0.30$ and 0.34 are shown in Fig. 3, along with those of a Te-doped sample ($x=0.30$) for comparison. The resistivity of the S-doped samples increases rapidly with decreasing temperature. These data were taken by slowly decreasing the temperature between data points and by allowing the samples to come to equilibrium. Identical results were obtained when measurements were made as the temperature was increased, i.e., no hysteresis effects were observed. If the samples are rapidly cooled to low temperature, a nonequilibrium condition results. To demonstrate this, sample 34S was immersed in liquid nitrogen in the dark, and the resistivity was measured immediately and then periodically for as long as the liquid-nitrogen supply

[20] D. B. Fitchen, Rev. Sci. Instr. 34, 673 (1963).

[21] W. Paul, G. B. Benedek, and D. M. Warschauer, Rev. Sci. Instr. 30, 874 (1959); P. J. Meltz, Ph.D. thesis, University of Illinois, 1966 (unpublished).

[22] G. E. Fenner, Phys. Rev. 134, A1113 (1964).

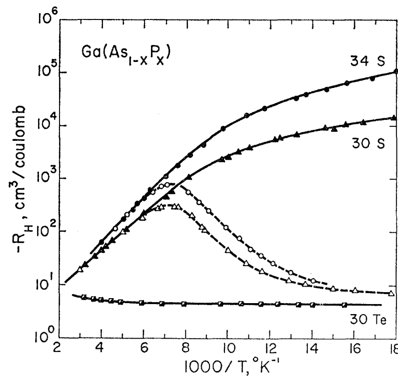

FIG. 4. Temperature dependence of Hall constant for typical S-doped $GaAs_{1-x}P_x$ crystals. The solid curves indicate measurements taken in the dark, and the dashed curves represent measurements taken with the sample under illumination.

lasted. The variation of the resistivity after the sample was cooled to 77°K is shown in Fig. 3. The dark resistivity is about one order of magnitude lower than that obtained in the original measurement, i.e., sample exposed to light. After 61 h and just before the liquid nitrogen was exhausted, the resistivity was still a factor of 3 lower than in the original measurement.

The Hall constants for these samples as a function of temperature are shown in Fig. 4. In this figure there are two sets of data for each sample. The solid curves and experimental points represent data taken in the dark in the same manner as the resistivity data just described. The dashed curves and open points represent data taken with the small lightbulb in the cryostat providing constant illumination of the sample. For sample 30Te the two sets of data were identical since the small normal photoconductivity was negligible on the scale of this figure. The solid data points indicate a continuous freeze-out of carriers as the samples are cooled. Although the ionization energy of the impurity level into which the carriers are being frozen cannot be accurately determined from the slope of the Hall-

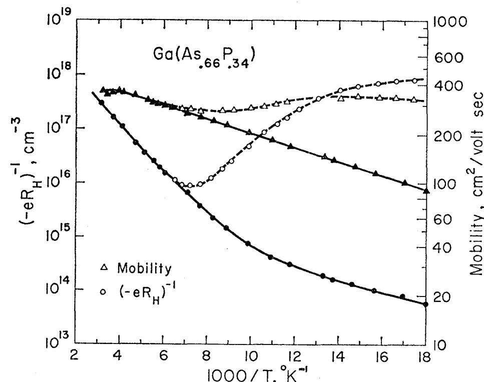

FIG. 5. Temperature dependence of Hall carrier concentration and mobility for a typical S-doped crystal. The solid curves indicate measurements taken in the dark, and the dashed curves represent data taken with the sample under illumination.

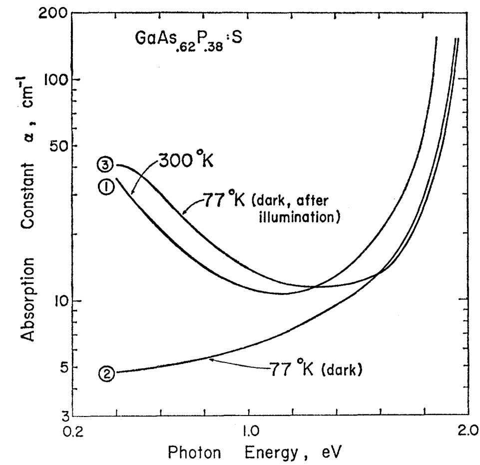

FIG. 6. Absorption data for S-doped $GaAs_{0.62}P_{0.38}$. Curve 1 was taken at 300°K, curve 2 was taken at 77°K after the sample had been cooled in the dark, and curve 3 was taken at 77°K after the sample had been exposed to a microscope lamp while it was cold.

constant curve, it appears that this energy is somewhat smaller for sample 30S than for sample 34S.

When these samples are irradiated with light after they have been cooled to a low temperature in the dark, the Hall constant decreases by about three to four orders of magnitude, indicating that a large increase in the free-carrier concentration occurs. At the same time the mobility increases appreciably, as is shown in Fig. 5 for sample 34S. The Hall carrier concentration calculated from $-1/eR_H$ is also shown for comparison. The increase in carrier concentration and mobility persists for a long time after the light is turned on, and then off, if the sample is maintained at low temperature. Only a small change could be observed after a period of several hours. If the sample was then warmed in the dark, considerable drift was observed. A gradual decrease in the number of the carriers occurred as the sample was warmed under illumination, reaching a minimum at about 140°K. From about 170°K to higher temperatures the results were the same with or without light.

The optical absorption as a function of photon energy for sample 38S is shown in Fig. 6. The method by which the optical absorption was measured has been described previously.[23] The data for curve 2 were obtained by first carefully shielding the cryostat from all stray light at room temperature and then cooling the sample over a period of about 30 min in the dark. After the sample was cold, the absorption measurements were made by scanning from long to short wavelengths. The data for curve 3 were taken after the sample was exposed to light from a microscope lamp while it was maintained at liquid-nitrogen temperature. The data for the room-temperature curve were taken in the usual manner. The absorption observed in the long-wavelength region has been previously shown to be due to free-carrier absorption for samples in the composition

[23] G. D. Clark and N. Holonyak, Jr., Phys. Rev. **156**, 913 (1967).

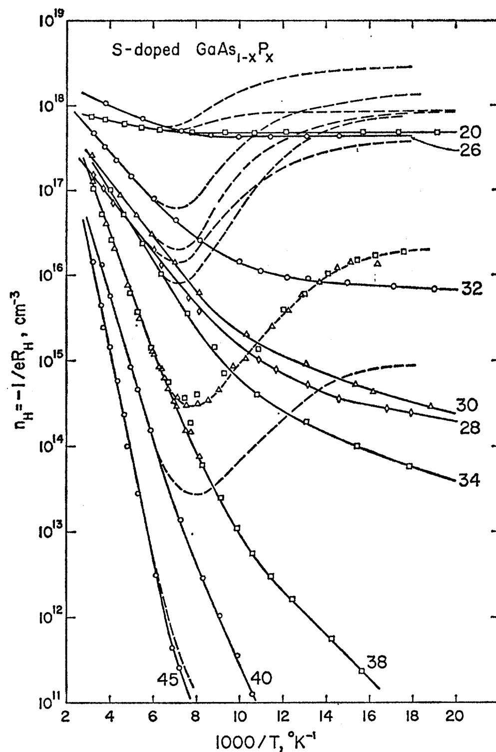

FIG. 7. Temperature dependence of Hall carrier concentration ($n_H=-1/eR_H$) for S-doped $GaAs_{1-x}P_x$ samples. The solid and dashed curves have the same significance as in Fig. 4. (Data points are omitted from some curves to avoid confusion.)

range $x\leq 0.50$.[23] Hence the large decrease in the absorption constant which is observed between the "300°K" and "77°K dark" curves is expected since the free-carrier concentration decreases by several orders of magnitude. After illumination of the sample at 77°K, the absorption constant increases to a value that is larger than that at room temperature. This is due to the large number of carriers that are photoexcited into the conduction band and which persists there because of their long lifetime. The small shift of the absorption edge toward shorter wavelengths after sample illumination at 77°K is due to the Burstein-Moss band-filling effect.

Variation with Composition

In both GaAs and GaP, S is incorporated into the lattice substitutionally at group-V sites. Although it has been pointed out that the carrier mobility in GaAs heavily doped with S in anomalously low and that the behavior of any group-VI donor can be complex in III-V compounds,[24] S acts essentially as a normal shallow donor in these materials. The behavior of S-doped $GaAs_{1-x}P_x$ crystals that has just been described is not characteristic of sulfur donor levels in either GaAs or GaP. Hence in the present work, Hall-effect and resistivity measurements were made on S-doped $GaAs_{1-x}P_x$ crystals throughout the crystal composition range to help characterize this impurity level. The results of these measurements over part of the composition range are shown in Fig. 7.

For samples with composition $x\leq 0.1$, S acts as a "normal" shallow donor, similar to Te-doped samples of low GaP concentration. Also, well-behaved *p-n* junction lasers can be made from this material, and no carrier freeze-out is observed. However, for samples with $x\geq 0.20$ the nonhydrogenic behavior of the impurity level introduced by S begins to appear, and as x increases, the magnitude of the carrier freeze-out increases. In samples of low composition x at low temperatures, the value of n_H when the sample is illuminated is larger than the room-temperature value. It is obvious from the n_H-versus-$1/T$ curves for these samples that the exhaustion region for these impurities occurs at temperatures well above 300°K, so that at low temperatures it is possible to excite carriers optically from impurity levels that are occupied at room temperature. For samples with $x>0.27$, n_H is no longer constant at low temperatures. For all of the samples the increase in n_H as the sample is cooled under illumination begins at about 125°K, and as x increases towards 0.45, the amount of increase over the minimum value under illumination generally decreases. Measurements could not be made on sample 45S (Fig. 7) below about 125°K because of its high resistance.

In the composition range $x\geq 0.45$ the crystals have an indirect band gap, but the behavior of the S impurity level is not drastically different from that just discussed. For example, for $x=0.60$ the behavior is very similar to that of Te-doped samples. The change in n_H from the room-temperature value to the value at low temperature under illumination for these samples is very close to the change in n_H for Te-doped samples of the same composition x between the same temperatures.

Analysis

Examination of the curves of Fig. 7 indicates that a complete analysis should include the effect of two levels, at least in part of the composition range. One level is relatively deep and causes the initial, large decrease in n_H, and the other is shallow. Measurements to lower temperatures would be needed, however, to determine the depth of the shallow level.

The analysis is complicated by the possibility of nonequilibrium conditions below about 110°K and by the lack of a detailed model for the deep impurity level. However, in the small temperature range which allows the determination of the ionization energy of the deep level, we can consider a model which consists only of a single impurity level and two conduction-band minima. For this case the charge-neutrality equation is

$$N_D-N_A=N_{c1}F_{1/2}(\eta)+N_{c2}F_{1/2}(\eta-\Delta E/kT)+N_D/\{1+0.5\exp[(-E_I-E_F)/kT]\}, \quad (1)$$

[24] F. V. Williams, J. Electrochem. Soc. **112**, 876 (1965).

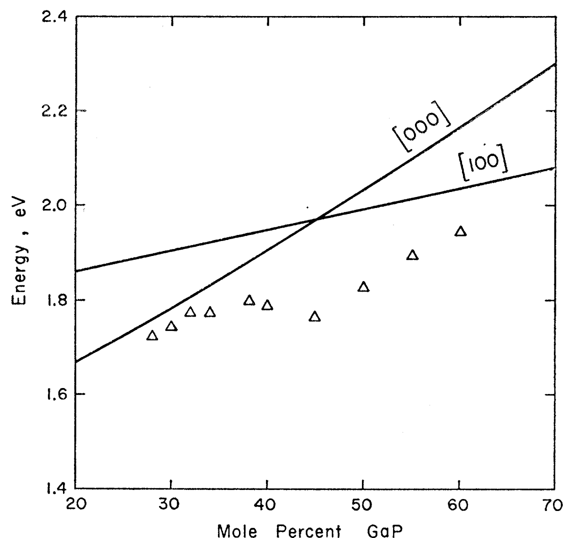

FIG. 8. Variation of the energy of the deep level in S-doped $GaAs_{1-x}P_x$ as determined by fitting the linear part of the n_H-versus-$1/T$ curves with the two-conduction-band model.

where N_D is the concentration of the deep levels and E_I is their ionization energy, N_A is the concentration of shallow acceptors, $\eta = E_F/kT$,

$$N_{c1} = 2(2\pi m_1 kT/h^2)^{3/2}, \quad N_{c2} = 2(2\pi m_2 kT/h^2)^{3/2},$$

$$F_{1/2}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1+\exp(\epsilon-\eta)},$$

and m_1 and m_2 are the density-of-states effective masses for the [000] and [100] conduction-band minima, respectively. The spin-degeneracy factor is taken to be 0.5, and the nonparabolic nature of the direct-conduction-band minima is neglected in this formulation.[2] From this equation and the values of the parameters from Sec. 2, computer calculations of the temperature dependence of the two-conduction-band Hall coefficient were made in which the values of N_D and E_I were adjusted to fit the experimental Hall-effect data in the linear part of the curves. The acceptor concentration N_A was also adjusted for best fit in the range 0–20% compensation. The energies of the levels resulting from this analysis are shown in Fig. 8 relative to the energies of the lowest conduction-band minima. The ionization energy is largest at the direct-indirect-transition point, but it is not obvious from the variation of the ionization energy that the impurity level observed is associated with a particular conduction-band minimum or set of minima.

5. PRESSURE MEASUREMENTS

Description of Model

The model that is used to analyze the pressure data of the Te-doped samples is similar to that of Bate.[10] In addition to the energy levels beneath the [000] minimum which have zero ionization energy, the donors are assumed to produce N_D levels of ionization energy E_D beneath and associated with the subsidiary [100] minima. Because of the large effective mass of the [100] minima, the donors form a distinct impurity level or a narrow impurity band beneath these minima. In addition, N_A shallow acceptors are assumed to be present in the crystals which provide compensation. Note that an increase in N_A has the effect of emphasizing the presence of the [100] donor level because it increases the ratio $N_D/(N_D-N_A)$ of the number of the levels to the number of available carriers. If we let n_1, n_2, and n_3 be the number of electrons in the [000] minimum, the [100] minima, and the [100] donor level, respectively, the total number of carriers can be expressed as

$$N = N_D - N_A = n_1 + n_2 + n_3 \tag{2a}$$

$$= N_{c1}F_{1/2}(\eta) + N_{c2}F_{1/2}(\eta - \Delta E/kT) + N_D/\{1+0.5\exp[(\Delta E - E_D - E_F)/kT]\}, \tag{2b}$$

where

$$\Delta E = \Delta E_0 - (\Delta E_0/x_c)x + (\partial \Delta E/\partial T)(T-300) + (\partial \Delta E/\partial P)P,$$

$$E_D = E_D(0) + (\partial E_D/\partial P)P,$$

E_F is the Fermi energy, ΔE_0 is the separation between the [000] minimum and the [100] minima in GaAs at 300°K and atmospheric pressure, and x_c is the phosphorus concentration at which the [000] and the [100] bands are equal in energy at 300°K. Also, $\partial \Delta E/\partial T$, $\partial \Delta E/\partial P$, and $\partial E_D/\partial P$ are the rates of change, assumed constant, of ΔE and E_D with temperature and pressure.

For a two-conduction-band semiconductor we can write the conductivity as

$$\sigma = 1/\rho = e(\mu_1 n_1 + \mu_2 n_2),$$

so that the normalized resistivity as a function of pressure can be written as

$$\rho(P)/\rho(0) = [\mu_1 n_1(0) + \mu_2 n_2(0)]/[\mu_1 n_1(P) + \mu_2 n_2(P)], \tag{3}$$

$$\rho(P)/\rho(0) = [b(0)n_1(0) + n_2(0)]/[b(P)n_1 + n_2(P)],$$

where $b = \mu_1/\mu_2$ is the mobility ratio of carriers in the two conduction bands. A large number of parameters clearly are involved in the model discussed above. Some are known from previous work, some are deduced from this work and are assumed to be the same for all samples, and some are unknown and are simply adjusted to give the best fit to the data for each individual sample. The energy separation ΔE_0 is assumed to be 0.36, in agreement with previous work.[2,11] The spin-degeneracy factor is taken to be 0.5. The rate of change $\partial \Delta E/\partial P$ of the separation between the [000] and the [100] minima with pressure will be assumed to be

[25] J. Feinleib, S. Groves, W. Paul, and R. Zallen, Phys. Rev. **131**, 2070 (1963).
[26] R. Zallen and W. Paul, Phys. Rev. **134**, A1628 (1964).

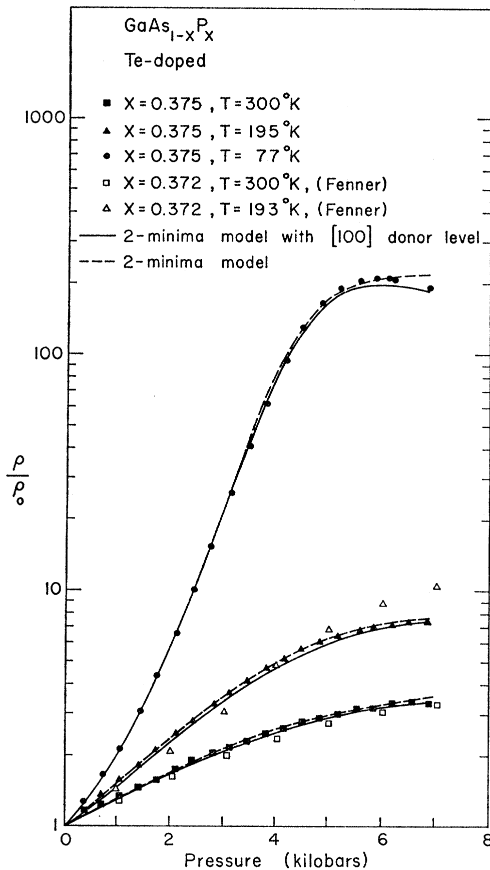

FIG. 9. Normalized resistivity versus pressure for a Te-doped $GaAs_{0.625}P_{0.375}$ sample. The dashed lines are calculated, on the basis of the two-minima model, for the following parameters: $b(300)=25$, $b(195)=44$, $b(77)=800$, $N_D=2.3\times10^{18}$ cm^{-3}, and $\partial\Delta E/\partial T=1.0\times10^{-4}$ eV/°K. The solid lines are calculated, on the basis of the two-minima model with a splitoff donor level, for the following parameters: $E_D=0.028$ eV, $b(300)=19$, $b(195)=27$, $b(77)=95$, $N_D=4.4\times10^{18}$ cm^{-3}, and $N_A=1.2\times10^{18}$ cm^{-3}.

11.5×10^{-3} eV/kbar, as measured in GaAs by Hutson, Jayaraman, and Coriell.[11] This value is reasonable because in GaAs the [000] minimum is known to move up at the rate of 10.7×10^{-3} eV/kbar,[25] and in GaP the [100] minima are known to move down at the rate of -1.1×10^{-3} eV/kbar,[26] implying that $\partial\Delta E/\partial P\approx11.8\times10^{-3}$ eV/kbar is in good agreement with the above result.

The behavior of the mobility ratio $b=\mu_1/\mu_2$ as a function of temperature and pressure can be estimated by means of data from Te-doped crystals of composition $x=0.20$ and $x>0.50$. The resistivity of sample 20Te changes by only a few percent throughout the experimental pressure and temperature ranges. Hence we assume that to a first approximation the mobility in the [000] minimum is independent of temperature and pressure. The Te-doped sample with $x=0.60$, which is well above the direct-indirect crossover, should have nearly all the carriers in the [100] minima. At 300°K this sample showed only 2% decrease in resistivity at 6.9 kbar. Therefore μ_2 is also assumed to be independent of pressure.

Measurements of the Hall coefficient and resistivity versus temperature for samples with $x\geq0.6$ indicate that the mobility remains relatively constant from room temperature to below 195°K, but then decreases steadily, so that at 77°K it is only $\frac{1}{4}$ to $\frac{1}{2}$ as large as it is at 300°K. A possible explanation of this decrease is that the electrons are frozen into a low-mobility impurity conduction-band tail at the bottom of the [100] minima. Since μ_1 is independent of temperature, the decrease of μ_2 has the effect of increasing the mobility ratio μ_1/μ_2 by a factor of 2 to 4 as the temperature is lowered to 77°K.

Combining the observed temperature and pressure dependence of the mobilities, we are able to write

$$b(P,T)=\mu_1(P,T)/\mu_2(P,T)\approx\mu_1(0,300)/\mu_2(0,T)=b(T),$$

where $b(T)$ is adjusted to give the best fit to the experimental data. For consistency with the experimental behavior of samples with $x\leq0.20$ and $x\geq0.60$, the mobility ratios which give the best fit must satisfy the relationship $b(300)\approx b(195)\approx\frac{1}{3}b(77)$. Furthermore, at 300°K the samples for $x<0.30$ have mobilities in the range 700–1000 cm^2/V sec, and samples for $x>0.50$ have mobilities in the range 30–60 cm^2/V sec, implying that $10<b(300)\approx b(195)<35$.

The rate of change with applied pressure, $\partial E_D/\partial P$, of the depth of the [100] donor level with respect to the [100] minima with which it is associated is expected to be quite small. In fact, if the wave function describing the splitoff donor energy level were truly characteristic of the band extrema with which the level is associated, then one would expect $\partial E_D/\partial P=0$. It must be remembered, however, that the donor level is degenerate with the [000] band minimum, and, since the matrix elements for scattering between the level and the minima are expected to be nonzero,[16] the behavior of the level will be perturbed. It is reasonable to expect that as the [100] minima and its associated donor level descend toward the [000] minimum with applied pressure, the effect of the perturbation will be to push the donor level upward toward the [100] minima. Samples with $x=0.40$ and $x=0.45$ (cf. Fig. 10, 77°K) exhibit a decrease in resistivity with increasing pressure as the [100] minima become lowest, indicating that the donor level becomes closer to the conduction band, and carriers are ionized from the level. Assuming that

$$1/\rho\propto n\propto\exp(-E_D/kT)$$

and

$$E_D(P)=E_D(0)+(\partial E_D/\partial P)P,$$

we can write

$$\ln[\rho(P)/\rho(0)]=(\partial E_D/\partial P)P(1/kT),$$

so that

$$\partial E_D/\partial P=kT(d/dP)\ln[\rho(P)/\rho(0)]. \quad (4)$$

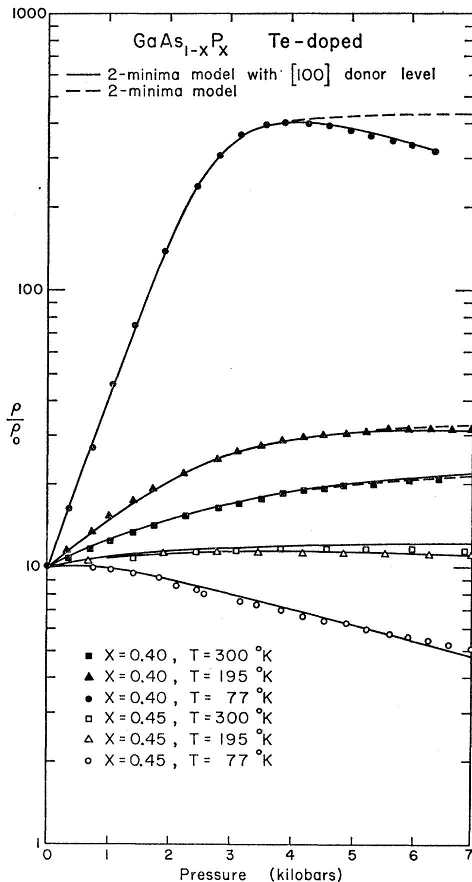

FIG. 10. Normalized resistivity versus pressure for a $GaAs_{0.60}P_{0.40}$ sample and a $GaAs_{0.55}P_{0.45}$ sample. The dashed lines are calculated on the basis of the two-minima model for the following parameters: $b(300)=17$, $b(195)=36$, $b(77)=940$, $N_D=2.1\times10^{18}$ cm^{-3}, and $\partial\Delta E/\partial T=1.2\times10^{-4}$ eV/°K. The solid lines were calculated on the basis of the two-minima model with a [100] impurity level. The parameters for the sample with $x=0.40$ are: $E_D=0.027$ eV, $b(300)=16$, $b(195)=20$, $b(77)=71$, $N_D=6.0\times10^{18}$ cm^{-3}, and $N_A=2.4\times10^{18}$ cm^{-3}. The parameters for the sample with $x=0.45$ are: $E_D=0.025$ eV, $b(300)=14$, $b(195)=19$, $b(77)=62$, $N_D=6.3\times10^{18}$ cm^{-3}, and $N_A=2.0\times10^{18}$ cm^{-3}.

Consequently the slope of the $\ln\rho/\rho_0$-versus-P curve gives $\partial E_D/\partial P$, which we find to be -1×10^{-3} eV/kbar. Since we do not know in detail how $\partial E_D/\partial P$ changes as a function of composition or of applied pressure, we simply assume that it remains constant.

The temperature parameter $\partial\Delta E/\partial T$ and the composition parameter x_c can be determined from the behavior of samples of composition $x=37.5$, 0.40, and 0.45, which all exhibit a maximum in the normalized resistivity-pressure curves (cf. Figs. 9 and 10). At higher pressures the resistivity decreases linearly on a $\ln\rho/\rho_0$-versus-P plot, and the slope is used to determine $\partial E_D/\partial P$ as discussed above. The pressure at which the maximum occurs increases with increasing temperature. Unfortunately, one cannot determine $\partial\Delta E/\partial T$ simply by measuring the pressure difference between the position of the maximum at two temperatures and by using the fact that $\partial\Delta E/\partial P$ is known. At the higher temperatures a large fraction of the donors is ionized, and the change in E_D at higher temperatures has a smaller effect on the resistivity than at lower temperatures. Consequently, the resistivity maximum would shift to somewhat higher pressures even if $\partial\Delta E/\partial T$ were zero. Similarly, one cannot determine the composition parameter x_c directly from the pressure at which the maximum occurs.

The "best" values of $\partial\Delta E/\partial T$ and x_c were obtained by substitution of different values of $\partial\Delta E/\partial T$ and x_c into the model until the resistivity maximum at each temperature occurred at the correct experimental pressure. The results based on this model are

$$x_c(300)=0.45\pm0.01\,,\quad 300°\text{K}$$
$$x_c(77)=0.43\pm0.01\,,\quad 77°\text{K}$$
$$\partial\Delta E/\partial T=(6\pm2)\times10^{-5}\ \text{eV/°K}.$$

The values obtained for x_c are in good agreement with Wolfe *et al.*,[27] who obtained $x_c\simeq0.45$ at 300°K by means of Hall measurements, with Fenner,[22] who found $x_c=0.44$ at 300°K from high-resistivity experiments, and with Cusano *et al.*,[28] who found $x_c=0.40$ at 77°K and $x_c=0.43$ at 300°K by studying recombination radiation. The value obtained for $\partial\Delta E/\partial T$ disagrees with the work of Zallen and Paul[26] on GaP, in which $\partial\Delta E/\partial T$ is found to be -6.0×10^{-5} eV/°K. However, the sign of $\partial\Delta E/\partial T$ obtained in the present work agrees with the results of Subashiev and Chalikyan,[29] who found $\partial\Delta E/\partial T=(15\pm8)\times10^{-5}$ eV/°K, and with the work of Fenner,[22] who found $\partial\Delta E/\partial T>1\times10^{-4}$ eV/°K.

To summarize, the parameters $E_D(0)$, N_D, and N_A, in addition to $b(300)$, $b(195)$, and $b(77)$, which were previously discussed, are adjusted with computer calculations to give the best fit to the data for each sample. The rest of the parameters and their dependence on composition, temperature, and pressure are experimentally determined, or are accepted as valid from previous work.

Analysis of Data: Te-Doped Crystals

Shown in Fig. 9 are the data for sample 37.5Te and, for comparison, the data of Fenner[22] for a Te-doped sample with $x=0.372$. The two sets of data are in good agreement in view of the fact that Fenner's sample is doped nearly twice as heavily as ours and has a slightly different composition.

Fenner was able to obtain a good fit to his data on the basis of the simple two-conduction-band model proposed by Ehrenreich.[2] He assumed that Boltzmann statistics were valid, that the mobility ratio $b=\mu_1/\mu_2$ was pressure-independent, and that the total number of

[27] C. M. Wolfe, N. Holonyak, Jr., C. J. Nuese, G. E. Stillman, M. D. Sirkis, and D. Hill, J. Appl. Phys. **37**, 434 (1966).
[28] D. A. Cusano, G. E. Fenner, and R. O. Carlson, Appl. Phys. Letters **5**, 144 (1964).
[29] V. K. Subashiev and G. A. Chalikyan, Phys. Status Solidi **13**, K91 (1966).

carriers $n=n_1+n_2$ in the direct and indirect bands remained constant throughout the pressure range (i.e., no carrier freeze-out occurred at high pressure).

We have also attempted to explain the behavior of sample 37.5Te on the basis of a two-minima model. The model and parameters used are as described in the previous section, with the exception that no donor impurity level is considered under the [100] minima. Thus Eq. (2a) becomes $N=N_D-N_A=n_1+n_2$. At the doping levels present in our samples it is necessary to use Fermi rather than Boltzmann statistics. The fitting parameters used are $b(300)$, $b(195)$, $b(77)$, N_D-N_A, and $\partial\Delta E/\partial T$. The best fit to the data is shown as the dashed curves in Fig. 9.

It is seen that an excellent curve fit to the pressure data can be obtained simply on the basis of the two-minima model. The only appreciable disparity between the calculated curves and the experimental-data curves occurs at 77°K at high pressures, where the experimentally measured resistivity begins to decrease. This is even more evident in sample 40Te, shown in Fig. 10. Again the two-minima model provides a good fit at low pressures but fails at higher pressures. Clearly, the data for sample 45Te which are also shown in Fig. 10 cannot be fit at any pressure by means of the two-minima model only.

With applied pressure and phosphorus concentrations such that the [100] minima are lower than the [000] minimum, all of the samples of this work exhibit a decrease in resistivity which is nearly linear on a $\ln\rho/\rho_0$-versus-pressure plot. The data indicate that the resistivity decreases as a result of carriers being thermally excited into the [000] conduction band, but that the energy levels from which the carriers come are associated with the [100] minima and not the [000] minimum. The rate at which the depth of these energy levels changes with pressure can be determined from the high-pressure slope of the data for sample 45Te shown in Fig. 10. We obtain $\partial E_D/\partial P=-1\times10^{-3}$ eV/kbar. If the levels were actually associated with the [000] minimum, one would expect a pressure coefficient of -11.5×10^{-3} eV/kbar. Furthermore, the magnitude and sign of our pressure coefficient agrees with the pressure coefficient found for the 0.54-eV gold level in silicon,[30] which has a band structure similar to that of GaP. The Au level in silicon is considerably deeper than the depth of the level observed here, which is typically 0.03 eV. However, a gold level in germanium with a depth of only 0.043 eV has been observed to have a pressure coefficient of 2.1×10^{-3} eV/kbar.[31] The sign difference is not surprising in view of the fact that the lowest conduction-band minima in Ge are in the [111] directions in k space instead of the [100] direction, as is the case for Si and GaP.

Another disturbing aspect of the analysis of our data based on the energy-band model involving only two

[30] M. I. Nathan and W. Paul, Phys. Rev. **128**, 38 (1962).
[31] M. G. Holland and W. Paul, Phys. Rev. **128**, 30 (1962).

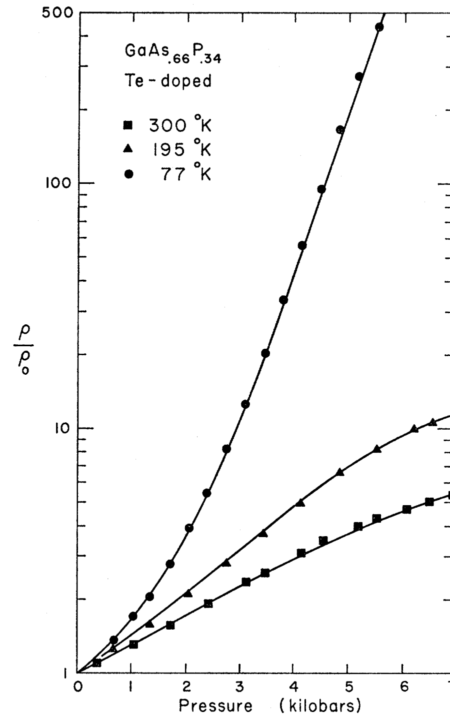

FIG. 11. Normalized resistivity versus pressure for a Te-doped $GaAs_{0.66}P_{0.34}$ sample. The solid lines are calculated on the basis of the two-minima model with [100] donor level for the following parameters: $E_D=0.038$ eV, $b(300)=18$, $b(195)=16$, $b(77)=90$, $N_D=3.5\times10^{18}$ cm^{-3}, and $N_A=2.1\times10^{18}$ cm^{-3}.

minima is the fact that the mobility ratio changes so drastically with temperature. As discussed earlier, based on the behavior of samples with $x<0.20$ and $x>0.60$, one would expect $b(77)/b(300)<5$, whereas the fit from the two-minima model indicates that $b(77)/b(300)>30$. Finally, the two-conduction-band model yields values for the Hall constants and change of resistivity with temperature which at 77°K are only in fair agreement with the experimental data. We conclude that the two-minima model is not adequate.

A more satisfactory explanation of the experimental data is achieved by resorting to the two-minima model with the addition of a donor impurity level beneath and associated with the [100] minima. This model gives an excellent fit to the data, as shown in Figs. 9–12, and is a convincing demonstration of the existence of these levels. Also, the resulting values of the mobility ratio at the temperatures considered are very reasonable. Furthermore, the values obtained for the Hall constant and change of resistivity with temperature are in good agreement with the experimentally obtained values. The mobility ratio $b=\mu_1/\mu_2$ stays consistently in the range 15–25 at 300°K and 15–30 at 195°K. At 77°K the mobility ratio is not accurately determined. The [100] donor level dominates the behavior of the resistivity, and the mobility ratio $b(77)$ can change from roughly 70 to 100 without producing a significant change in the values obtained for the parameters. The

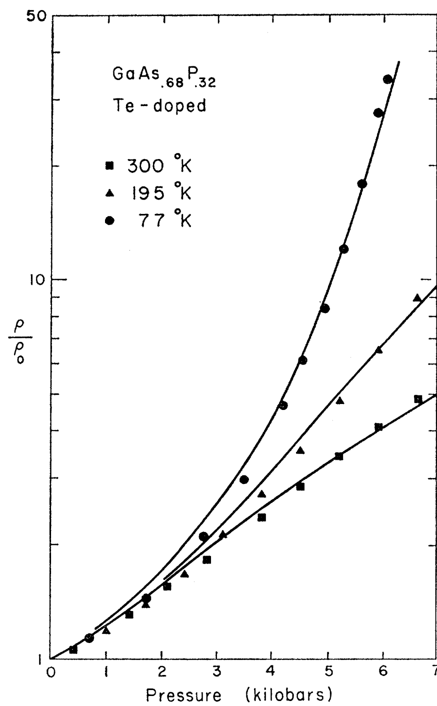

FIG. 12. Normalized resistivity versus pressure for a Te-doped $GaAs_{0.68}P_{0.32}$ sample. The solid lines are calculated on the basis of the two-minima model with a [100] donor level for the following parameters: $E_D=0.031$ eV, $b(300)=16$, $b(195)=20$, $b(77)=89$, $N_D=2.1\times10^{18}$ cm^{-3}, and $N_A=0.5\times10^{18}$ cm^{-3}.

depth of the donor level beneath the subsidiary band minima is 0.025–0.038 eV and decreases somewhat with increasing phosphorus concentration. This is a result of the fact that the [000] minimum exerts a perturbing effect on the donor level and tends to push it up towards the [100] minima.

The validity and importance of our assumptions concerning the parameters b and m_1 were tested by attempting to fit the data for sample 40Te by using different pressure and composition dependences for these parameters. First, b and m_1 were chosen to be functions of pressure based on the pressure dependence of sample 20Te. The resulting values of the fitting parameters were very slightly different from those determined assuming b and m_1 to be pressure-independent. Next, m_1 was assumed to be composition-independent, i.e., $m_1=0.072m_e$. A reasonably good fit to the data was achieved, and the resulting value of E_D remained unchanged. Therefore, it is possible to conclude that the basic results of this work concerning the position and pressure dependence of the splitoff donor level are independent of the exact choice made for the pressure and composition dependence of b and m_1. It can be seen in Fig. 12 that the curve fit to the data for sample 32Te is somewhat unsatisfactory at low pressures. The probable explanation is that in this composition and pressure range the higher-lying [100] minima and their associated donor level are less dominant than they are for higher compositions and pressures. As a result, the variation of the mobility and effective mass with pressure, which are not included in the model, become more important.

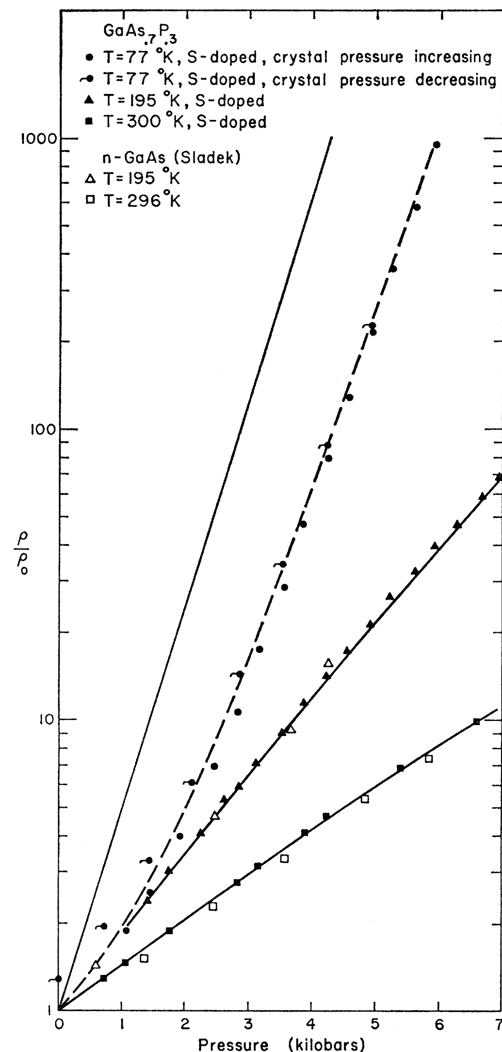

FIG. 13. Normalized resistivity versus pressure for a $GaAs_{0.70}P_{0.30}$ sample. The solid lines correspond to the model used to fit the 300 and 195°K data. The steep straight line at the left of the figure corresponds to the same model at 77°K, which clearly does not fit the 77°K data. The dashed line corresponds to the model with the shallower level used only at 77°K. (See text.)

Analysis of Data: S-Doped Crystals

The data for sample 30S are shown in Fig. 13. The behavior of the sample at 300 and 195°K is similar to the behavior of samples 28S and 32S. The 300 and 195°K pressure data and the Hall-coefficient and resistivity-versus-temperature data can be fit by means of the two-conduction-band, one-donor-level model previously described. Since the [100] minima have a relatively small effect at this composition, a simple one-conduction-band, one-donor-level model yields a

good estimate of the pressure coefficient and gives a reasonable fit to the data. The 77°K pressure data are not considered in the immediate analysis. The fit to the pressure data shown in Fig. 13 corresponds to $b(300)=30$, $b(195)=30$, $E_D=0.16$ eV, $N_D=1.9\times10^{19}/\mathrm{cm}^3$, $N_A=2.6\times10^{18}/\mathrm{cm}^3$, and a pressure coefficient with respect to the [000] minimum of 10.8×10^{-3} eV/kbar. The pressure coefficient is determined from the low-pressure portion of the 195°K curve which is nearly linear. The 300 and 195°K curves are seen to be a good fit, but the 77°K curve does not fit. If our model were correct at all temperatures, we would expect the 77°K data to fit even though they were not specifically included in the curve-fitting routine. The reason that the 77°K data fail to fit is discussed below.

The donor ionization energy E_D is ~0.16 eV below the *indirect* minima. This ionization energy is greater than one would expect from existing theories, if the level is closely associated with the [100] minima. Since ΔE, the energy separation between the [000] and the [100] minima, is 0.12 eV at 300°K for $x=0.30$, we observe that the S donor level has a depth of 0.04 eV and, as mentioned above, a pressure coefficient of 10.8×10^{-3} eV/kbar with respect to the [000] minimum. This pressure coefficient agrees very well with the observed coefficient for the energy gap $\partial E_g/\partial P=(10.7\pm0.3)\times10^{-3}$ eV/kbar,[25] which suggests the possibility that the level is actually associated with the valence band and not with the [100] minima. Experimental evidence on Ge and Si exists which shows that deep donor levels have a tendency to have a small pressure coefficient with respect to the valence bands.[30,31]

Sladek[32,33] has studied n-type GaAs samples containing nonshallow donors whose pressure behavior is very similar to the behavior of our $GaAs_{1-x}P_x$ samples with $0.28<x<0.32$. The data for one of Sladek's samples are shown in Fig. 13. The agreement with the data here is seen to be quite good, the only appreciable difference being that our data show a slight roundoff at high pressure because of the proximity of the [100] minima. The data of Sladek which are shown are actually normalized Hall-effect-versus-pressure measurements, but since the pressure dependence is due to a change in the number of charge carriers, we expect the Hall constant and the resistivity to behave similarly. The agreement between the high-pressure $GaAs_{0.70}P_{0.30}$ data of this work and the high-pressure GaAs data of Sladek reflects the fact that the pressure coefficients are nearly the same. However, since the depth of the levels involved is large compared to kT, the behavior of the samples as a function of temperature must be studied to determine the level depth. Sladek found the level depth to be 0.17 eV and the pressure coefficient to be $10.2\pm1.0\times10^{-3}$ eV/kbar. Sladek[33] considers the possibility that the nonshallow donors are levels associated with the [100] minima, but points out that according to the existing theory,[15–17] such levels should remain close to the minima with which they are associated. He concludes that the levels which he observes are probably due to carbon, nitrogen, or oxygen impurities.

Paul,[34] however, suggests that the levels observed by Sladek are associated with higher-lying minima, because levels deeper than 0.17 eV have been studied in GaAs[25] and have been observed to have much smaller pressure coefficients with respect to the conduction band. Furthermore, Kosicki, Paul, Strauss, and Iseler[13] have done high-pressure work on S-doped GaSb and explain their data by means of a donor level which is 0.34 eV below the [100] minima with which it is associated. However, the data of Kosicki *et al.* could also be satisfactorily explained by means of a level which is nearly fixed with respect to the valence band.

At 77°K the resistivity of sample 30S increases by three orders of magnitude in less than 6 kbar, as seen in Fig. 13. We also observe that the data points taken with pressure decreasing fall slightly above those taken with pressure increasing. Since the high-pressure slope is very nearly a straight line, we assume that the behavior of the sample is dominated by an impurity level and that at this temperature we can completely neglect the presence of the higher-lying minima.

From the high-pressure slope of the line in Fig. 13 we can calculate the pressure coefficient of the energy level with respect to the [000] minimum. The result is $9.8\pm0.2\times10^{-3}$ eV/kbar. The accuracy of this result is somewhat questionable because the resistivity continuously drifts upward as the pressure increases, and drifts downward as it decreases. After a change in the pressure, it was necessary to wait 15–30 min before data were taken. After this time interval the rate of drift had decreased appreciably, but still had not stopped. Values of the pressure coefficient ranging from 9.6 to 10.4×10^{-3} eV/kbar have been calculated for various S-doped samples. We conclude that the pressure coefficient of the level which dominates the behavior of our samples at 77°K is $(10.0\pm0.4)\times10^{-3}$ eV/kbar.

The above pressure coefficient is somewhat smaller than the pressure coefficient of $(10.8\pm0.3)\times10^{-3}$ eV/kbar obtained at 195 and 300°K. Furthermore, the 77°K data clearly do not fit the calculated curve obtained from the model used to fit the 195 and 300°K data. A fit to the 77°K data obtained from our basic two-minima, one-level model is shown as the dashed curve in Fig. 13. The corresponding parameters are $N_D=1.9\times10^{19}/\mathrm{cm}^3$, which is chosen to agree with the value determined at 300 and 195°K; $N_A=1.8998\times10^{19}/\mathrm{cm}^3$, which is determined by the Hall constant at 77°K; and $E_D=0.06$ eV, which is the level depth

[32] R. J. Sladek, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Duond Cie., Paris, 1964), p. 546.

[33] R. J. Sladek, Phys. Rev. **140**, A1345 (1965).

[34] W. Paul, discussion in Ref. 32.

beneath the [100] band minima and is chosen to give the best fit to the experimental pressure curve. The fit obtained is nearly independent of N_D and is not strongly dependent on N_D-N_A as long as $(N_D-N_A)/N_D$ is less than 0.1 (sample heavily compensated). However, the fit is quite sensitive to changes in E_D because the level is still above the [000] band minimum. The mobility ratio is not involved, because at 77°K a negligible number of carriers is in the higher-lying minima. Thus the level which dominates the behavior of the samples at 77°K is shallower and has a different pressure coefficient than the 0.16-eV level observed at 195 and 300°K.

At 195 and 300°K the 0.16-eV level predominates, and the behavior of the samples is relatively unaffected by the presence of the shallow level. At 77°K, however, the 0.16-eV level must for some unknown reason be unable to absorb carriers, and the result is that the shallow level becomes important in determining the high-pressure behavior of the sample resistivity. From this it follows that the deep 0.16-eV level is the level that gives rise to the persistent light-sensitive behavior observed at low temperature. At 77°K the level is effectively nonexistent. Its only effect is to accept "reluctantly" a few carriers as the pressure increases and release them as the pressure decreases, giving rise to the observed hysteresis. Since the resistivity tends to drift slowly downward after a decrease in pressure, we conclude that more of the deep levels are full at high pressure than at atmospheric pressure, when the sample is in equilibrium. Furthermore, at high pressure the samples seem to equilibrate more rapidly than at low pressure.

In the pressure vessel used in this work the samples were cooled quite rapidly, and as a result some of the deep donor levels did not have a chance to fill. If the samples could have been cooled over a period of hours, so that equilibrium effectively maintained, the hysteresis would presumably be somewhat smaller. The hysteresis effect is most evident in samples in the range $0.20<x<0.28$. At 77°K for a crystal composition of $x=0.26$ the [100] band minima are 0.14 eV above the [000] minimum. Consequently, the [100] donor level is $\sim$0.08 eV above the [000] minimum and has little effect on the pressure dependence of the sample, thus allowing the hysteresis to play a major role. For values of $x>0.27$, however, the 0.06-eV level becomes dominant, causing a large resistivity increase with applied pressure. Two samples measured with $x=0.1$ exhibited a very small hysteresis effect. It is possible to explain this small effect by assuming that the deep S level is a second level $\sim$0.16 eV beneath the [100] band minima. For $x=0.10$ the level would be too far above the [000] minimum to have an appreciable effect.

In order to verify the idea that two separate types of levels exist, the following experiment was performed. A S-doped sample of composition $x=0.30$ and a

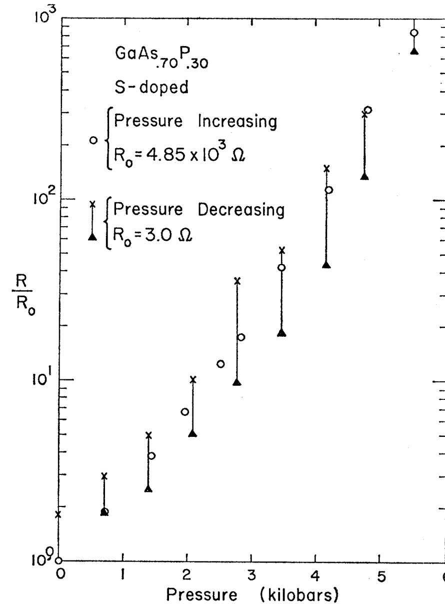

FIG. 14. Normalized resistivity versus pressure for a S-doped $GaAs_{0.70}P_{0.30}$ sample. The pressure-increasing curve (open circles) is taken in the dark. The pressure-decreasing curve (closed triangles and crosses) is taken with the sample illuminated. The curves are actually shifted three orders of magnitude in resistance. The resistance at atmospheric pressure is 4.85×10^3 Ω for the pressure-increasing curve and $\sim$3 Ω for the pressure-decreasing curve. (See text.)

$GaAs_{0.67}P_{0.33}$ light-emitting diode were mounted side by side on the same header and inserted in the pressure vessel. At room temperature the sample had a resistance of several ohms. First, the sample was cooled in the dark, causing an increase of the sample resistance to $\sim10^3$ Ω, and supposedly nearly filling the 0.16-eV impurity levels. With the sample still in the dark, the pressure was raised to 6 kbar, leading to an increase of the resistance to $\sim10^6$ Ω, which is due to filling of the shallow impurity level. Next, the light-emitting diode was flashed, which in turn caused the sample resistance to drop to $\sim10^3$ Ω. The diode could not be left on, because it heated the sample. At this point, presumably the deep levels were emptied. The majority of the carriers freed by the light were immediately bound to the shallow level, which, as a result of the 6-kbar pressure, was $\sim$0.02 eV below the direct minimum. The pressure was then lowered.

According to our model, lowering the pressure should allow the shallow level to move back up to its original position above the [000] minimum. As the level moves up, it should "spill" carriers back into the [000] minimum, leading then to a reduction in sample resistance to a few ohms, or roughly its original value at 300°K and atmospheric pressure. Furthermore, the shape of the curve should be similar to the shape of the curve when the pressure was increased in the dark, because the curve shape is not strongly dependent on the number of carriers. The two curves, however,

should be shifted roughly three orders of magnitude in resistance.

The results of the experiment can be seen in Fig. 14. The open circles correspond to increasing the pressure in the dark. The decreasing-pressure curve presented some problems, because after the diode was flashed, the resistance tended to drift appreciably at the rate of approximately a 5%/min increase in resistance. This drift, which was much larger than that observed when the samples were not illuminated, was apparently due to the greatly increased number of empty 0.16-eV levels. In addition, because of transient thermal effects, it was necessary to wait ~30 sec before taking an experimental reading. The first reading taken at each pressure is denoted in Fig. 14 by a solid triangle. The resistivity drifted upwards for a period of ~20 min to the value denoted by a cross. The pressure was then lowered in the dark, and at the new pressure the diode was again flashed and the process repeated.

The two curves agree reasonably well, indicating that there are two types of levels. It is also clear that the shallow levels must be present in concentrations $\geq N_D$, because at high pressure with the light on, nearly all the carriers are in the shallow level. This rules out the possibility that the level is due to the presence of a second impurity, such as Si, which might be present to concentrations of $\sim 10^{16}$ cm^{-3}. Such a level could conceivably become important at 77°K in the dark because most of the carriers would be frozen into the 0.16-eV impurity level.

Composite Curves

One way of obtaining an over-all view of how the donor levels described above affect the high-pressure behavior of $GaAs_{1-x}P_x$ is to construct composite curves of the data. By making use of the parameters determined in previous sections, we can write the separation ΔE between the [000] and the [100] minima as

$$\Delta E(P,x,T) = 0.36 - 0.80x - 11.5(10^{-3})P + 6.0(10^{-5})(T-300),$$

where x is the mole fraction of GaP, P is the pressure in kilobars, T is the temperature in degrees Kelvin, and $\Delta E(P,x,T)$ is expressed in electron volts. If we assume that the effect of pressure on $GaAs_{1-x}P_x$ is similar to the effect of changing the crystal composition x and that pressure and composition are related by the above equation, then changing the composition by 1% should be equivalent to applying a pressure of $P \approx 0.70$ kbar. This idea has been used previously to relate Gunn-effect thresholds obtained from high-pressure work on GaAs to those obtained for $GaAs_{1-x}P_x$ of equivalent composition.[35]

Following the above line of reasoning, we can combine the $GaAs_{1-x}P_x$ high-pressure data into one com-

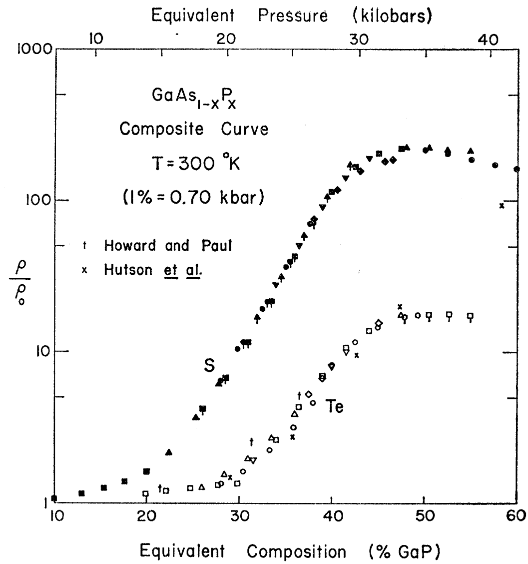

FIG. 15. Composite curves of S- and Te-doped $GaAs_{1-x}P_x$ data at 300°K. Samples from the range $0.1 \leq x \leq 0.5$ are included. The data points corresponding to a given sample can be determined using the lower (composition) scale. The upper (equivalent-pressure) scale gives the equivalent pressure required for GaAs. Some points taken from the high-pressure GaAs data of Hutson, Jayaraman, and Coriell (Ref. 11) and Paul (Ref. 36) are included for comparison. (See text.)

posite curve for each temperature and dopant, which should resemble the behavior of GaAs under very high pressure. The composite curves obtained from our data at 300 and 77°K are shown in Figs. 15 and 16. Also shown for comparison at 300°K are several data points from the high-pressure GaAs data taken by Hutson *et al.*[11] and by Howard and Paul.[36] The curves shown were constructed by starting with the data for the sample with the lowest phosphorus concentration, which for the case of the S-doped material was a sample with $x = 0.10$. These data were normalized so that at atmospheric pressure they agreed with the data of Hutson *et al.*[11] at 7 kbar. The resulting values were plotted to a pressure of 14 kbar. Next, the data of the sample for $x = 0.20$ were normalized so that at atmospheric pressure they agreed with the $x = 0.10$ sample at 7 kbar.

In this fashion the data of the samples with increasing values of x were in each case normalized to give the best fit to the pertinent portion of the curve. The equivalent phosphorus concentration is given at the bottom of the curves, and the equivalent pressure on GaAs is given at the top. Different symbols are used for the data from adjoining samples, so that by using the equivalent phosphorus-concentration scale, one can tell which sample contributed a given datum point. The samples used in this work are much more heavily doped than the GaAs used by Hutson *et al.*[11] or by Howard and Paul,[36] and as a result of band filling, the point at which the resistivity begins to increase sharply

[35] J. W. Allen, M. Shyam, Y. S. Chen, and G. L. Pearson, Appl. Phys. Letters **7**, 78 (1965).

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

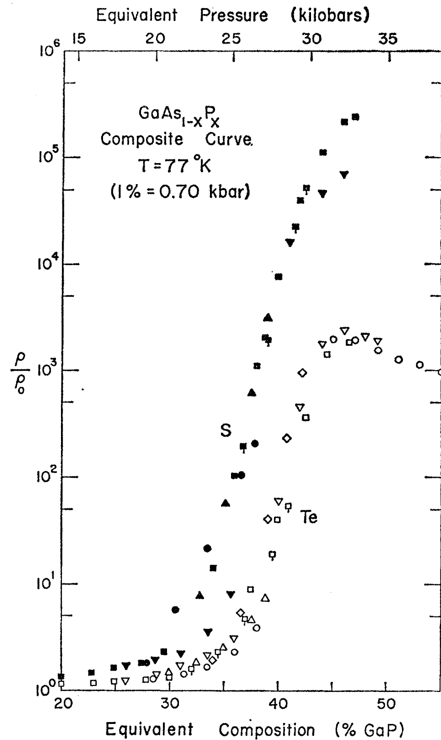

FIG. 16. Composite curves of S- and Te-doped $GaAs_{1-x}P_x$ data at 77°K. Samples from the range $0.2 \leq x \leq 0.45$ are included. The data points corresponding to a given sample can be determined using the lower (composition) scale. The upper (equivalent-pressure) scale gives the equivalent pressure required for GaAs.

is shifted to lower pressure. Consequently, we can expect only qualitative agreement with the GaAs data.

The data from S-doped crystals and from Te-doped crystals both form reasonably smooth curves, with some deviation occurring in the region where the resistivity changes abruptly with pressure. At both 300 and 77°K the data of the S-doped crystals exhibit a rapid increase in resistivity at a lower pressure (or composition) than do the Te-doped samples. Furthermore, the magnitude of the change in resistivity is greater for the S-doped material. The normalized resistivity reaches a maximum of ~ 200 at 300°K and $\sim 3\times 10^5$ at 77°K for the S-doped samples, compared with a maximum of ~ 20 and $\sim 2\times 10^3$ at 300 and 77°K, respectively, for the Te-doped samples. Since we know that the mobility ratio at room temperature is $b(300) \approx 20$, we conclude that carrier freeze-out at high pressure has little effect on the Te-doped samples at 300°K, but has a large effect on the S-doped samples. At 77°K carrier freeze-out dominates the behavior of both the S-doped and the Te-doped samples.

The rapid resistivity increase which occurs at lower pressures in S-doped than in Te-doped material plus the greater increase of ρ/ρ_0 in the S-doped material are a direct result of the fact that the ionization energy of the [100] donor level is greater for $GaAs_{1-x}P_x$ doped with S than with Te. By studying the 77°K composite

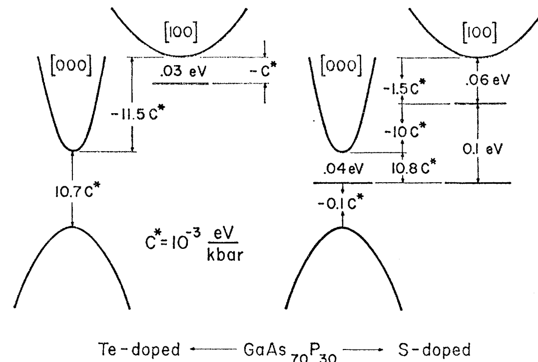

FIG. 17. Schematic diagram of the energy-band and splitoff-level structure for S- and Te-doped $GaAs_{0.70}P_{0.30}$. The pressure coefficients shown have the units 10^{-3} eV/kbar.

curve, we can estimate how much greater E_D is in the S-doped material. We observe that the region of resistivity increase occurs at a pressure roughly 3.1 kbar lower in S-doped material than in Te-doped material. We know that 3.1 kbar corresponds to a change in ΔE of approximately 0.035 eV, so we estimate that the S donor is ~ 0.035 eV deeper than the Te donor. This is consistent with our previous results of $E_D = 0.06$ and 0.03 eV for the S- and Te-doped material, respectively. We recall that the deep 0.16-eV level occurring in S-doped material is frozen-out and not visible at 77°K.

6. DISCUSSION

The good agreement between the experimental resistivity-versus-pressure measurements and the calculations based on a model which includes two conduction bands *and* the impurity levels associated with the [100] band minima is strong evidence that in both S- and Te-doped material these levels have a pronounced or even dominant effect on the properties of $GaAs_{1-x}P_x$ near the direct-indirect transition. A schematic diagram of the energy bands and their associated donor levels is shown in Fig. 17. The shallower of the two S levels, which become visible only at 77°K, has an estimated depth of 0.06 eV beneath the [100] minima for $x = 0.30$ and is apparently analogous to the 0.03-eV level observed in the Te-doped crystals.

The pressure coefficient of the 0.06-eV S donor level with respect to the [100] band minima is -1.5×10^{-3} eV/kbar. This is slightly larger than the pressure coefficient of -1×10^{-3} eV/kbar observed for the Te donor. It is not surprising, however, that the deeper level has a slightly larger pressure coefficient, because it is strongly perturbed by the presence of the [000] direct-band minimum. As the level is pushed closer to the [100] band and exhibits more nearly the properties of a "hydrogenic" impurity, we would expect the pressure coefficient to decrease to that of the band edge. Furthermore, the pressure coefficient for the Te donor level was determined by the behavior of the resistivity above the direct-indirect crossover. If the

coefficient could be accurately determined below the crossover, as it can for the deeper-lying S donor, it might be found to be somewhat larger.

In Te-doped crystals at 77°K and $x=0.40$ the donor level associated with the [100] minima has roughly the same energy as the [000] minimum, and for $x>0.40$ it lies at an energy lower than the [000] minimum. It is interesting to note that the largest x at which it has been possible to attain stimulated emission in $GaAs_{1-x}P_x$ is $x\approx 0.40$.[7] One would not expect laser action to be possible when the donor level associated with the [100] minima is lower than the [000] minimum, because electron transitions from this level would provide a competing nonradiative recombination process. Therefore, we would expect $x\approx 0.40$ to be the largest value for which stimulated emission could occur, which agrees well with the experimental result. We remark that it would require a pure crystal to allow the [100] minima to dominate the direct-indirect transition and to show its intrinsic position (composition x) at low temperature. However, only doped crystals are used for laser *p-n* junctions, and the direct-indirect transition and quenching of stimulated emission is most likely always due, at least in part, to the donor impurity associated with the [100] minima.

For S-doped crystals at 77°K the 0.06-eV level will be at the same energy as the [000] minimum when $x\approx 0.36$. This implies that the largest x at which stimulated emission would be expected to occur in S-doped material is $x=0.36$. However, the largest x attained thus far for a S-doped laser diode has been only 0.33.[6]

The physical characteristics of the deep impurity center introduced by S-doping suggest two possible explanations or models to describe the unusual behavior that is observed. One possibility is that S is incorporated into the lattice substitutionally throughout the crystal-composition range and that the behavior observed is characteristic of S donor levels which are associated with the higher-lying [100] minima. The other possibility is that the defect, which has the properties of a double-acceptor center,[37,38] is not due to the S donor directly, but results from a complex involving S and perhaps some other impurity or native defect. However, in either case, it must be concluded that the S atom is the dominant source of the various levels since none of the Te- or Se-doped samples, which were prepared from the same starting materials in exactly the same manner, exhibited this type of behavior.

The 300°K composite curve for the S-doped samples shown in Fig. 15 is of particular interest because at 300 and 195°K the behavior of the S-doped samples is dominated by the deep level. The curve contains data from every S-doped sample measured in the composition range $x\leq 0.50$. The curve is seen to be extremely well defined. This implies that there is a very systematic variation of the pressure dependence as a function of composition. The shape of the composite curve is what would be expected if the deep S level is associated with the [100] band minima. Iseler and Strauss[39] suggest that because of the different symmetries of the lowest conduction-band minimum and the subsidiary donor levels which were shown to be associated with the [100] minima, the cross section for scattering electrons from the conduction band to the donor levels might be sufficiently small to account for the long lifetime of the nonequilibrium conduction-band electrons. Theoretical calculation of the scattering cross section is impractical because of the lack of knowledge of the subsidiary donor wave functions. If the difference in symmetries of the lowest conduction-band minima and the subsidiary donor level is the cause of the long lifetime of the conduction-band electrons, then the long-lifetime effects should disappear when the composition is changed so that the conduction-band minima with which the energy level is associated are lowest. It is observed, however, that the persistent light effect is plainly visible for compositions as high as $x=0.80$. This result cannot be easily reconciled with the model proposed by Iseler and Strauss.

The long lifetime of the nonequilibrium conduction-band electrons and the large photosensitivity which exist in S-doped $GaAs_{1-x}P_x$ samples for $x>0.45$ suggest that the effect could be due to a double-acceptor center. This behavior is similar to that observed in Au-, Fe-, or Mn-doped Ge,[37] except that in the present case the lifetime of photoexcited carriers is much longer. Similar centers were first observed in compound semiconductors by Lorenz and Woodbury in CdTe[38] and were attributed to interaction of native defects with impurities. The behavior of S-doped $GaAs_{1-x}P_x$ samples can be understood in terms of this model by assuming that a large number of the S impurity atoms are incorporated into the lattice, as expected of a shallow donor. In the GaAs-rich part of the composition range these normal shallow donors form an impurity band which overlaps the conduction band, so that there is no carrier freeze-out into the donor states. In the GaP-rich part of the composition range the normal donor levels are deeper and cause carrier freeze-out. However, some of the S atoms may form complexes with other impurities or vacancies and thereby provide the double-acceptor centers. Each of the double-acceptor centers would then accept one electron in the first charge state at room temperatures and below, and at low temperatures a large number of the centers become doubly negatively charged. When such a sample is at low temperatures and is illuminated with light capable of producing

[37] W. C. Dunlap, Jr., Phys. Rev. **97**, 614 (1955); W. N. Tyler and H. H. Woodbury, *ibid.* **102**, 647 (1956).

[38] M. R. Lorenz and H. H. Woodbury, Phys. Rev. Letters **10**, 215 (1963); M. R. Lorenz, M. Aven, and H. H. Woodbury, Phys. Rev. **132**, 143 (1963); M. R. Lorenz, B. Segall, and H. H. Woodbury, *ibid.* **134**, A751 (1964).

[39] G. W. Iseler and A. J. Strauss, Bull. Am. Phys. Soc. **12**, 404 (1967).

electron-hole pairs, the holes are quickly trapped by the doubly negatively charged center, leaving an extra electron in the conduction band and leaving the double-acceptor center in its singly charged state. Since the center is still singly charged negatively, it presents a Coulomb barrier to the electrons in the conduction band. Because of the low temperature, the recombination of the electron-hole pairs at the double-acceptor center is very slow, resulting in the persistent increase in carrier concentration observed experimentally. At the same time, if the mobility is limited by ionized impurity scattering, it should show a significant increase as a large number of centers are converted from doubly negatively charged to singly negatively charged states. This could explain the mobility increase observed experimentally. However, since the mobility is not simply limited by ionized impurity scattering, a comparison of the magnitude of the increase with theory cannot be made.

In spite of certain attractive features of the double-acceptor model, we remark that the nature of the impurity or complex involved in the double-acceptor center, the reason for the regular variation in the concentration, and especially the large pressure coefficient associated with the (assumed) complex, are not accounted for by the double-acceptor model.

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Landau Levels in Uniaxially Stressed Zinc-Blende-Type Semiconductors

Jan Blinowski
Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

and

Marian Grynberg
Institute of Physics, University of Warsaw, Warsaw, Poland

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The energies and wave functions of a few first valence-band Landau levels in zinc-blende-type semiconductors subjected to a high uniaxial stress parallel to the magnetic field in the [111] and [001] crystal directions are calculated analytically by a simple perturbation method, which cannot be applied in the case of non-deformed crystals. The selection rules and relative strengths for direct dipole interband transitions are presented. As was pointed out by Bell and Rogers, at low magnetic fields the presence of the linear-k terms in the effective-mass Hamiltonian introduces remarkable changes in the energy spectrum and selection rules. It is shown that the strengths of the transitions induced by these terms can have a magnitude comparable to the strengths of the other transitions. Therefore, one can expect that magneto-optical experiments on stressed crystals should give the value of Kane's constant K as well as other valence-band parameters. The situation in stressed crystals is more convenient than in unstressed ones because the number of transitions at the absorption edge is smaller and the theoretical description is less complicated.

1. INTRODUCTION

As was shown by Parmenter,[1] Dresselhaus,[2] and Kane,[3] the lack of inversion symmetry in zinc-blende-type crystals (space group T_d) can introduce terms linear in $\mathbf{k}$ into the effective-mass Hamiltonian for Γ_8 valence bands. Because of these terms, the maxima of the uppermost valence bands are no longer located at the Γ point, but away from it in the [111] crystal direction. The energy surfaces in the vicinity of the maxima are prolate ellipsoids. The energy of the maxima relative to Γ was estimated by Kane to be of the order of 10^{-4} eV in InSb.

There are no experimental data directly confirming such a model. The one feasible method to prove it could be provided by magneto-optical (interband as well as intraband) experiments.

Pidgeon and Brown, in their theory of interband magnetoabsorption phenomena in InSb at high magnetic fields,[4] neglected the linear terms as small in comparison with the other terms in the Hamiltonian.

[1] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).
[2] G. Dresselhaus, Phys. Rev. **100**, 580 (1955).
[3] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
[4] C. R. Pidgeon and R. N. Brown, Phys. Rev. **146**, 575 (1966).