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Pressure Effect on Resistivity of Ga$(As_{1-x}P_x)$

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The change of resistance of n-type Ga$(As_{1-x}P_x)$ samples under hydrostatic pressure up to 15 000 atm was measured between 190 and 363°K. Large pressure-dependent resistance changes were observed for samples with $x\approx0.35$. These observations are consistent with the presence of another conduction band edge of much lower mobility presumably along $k=(100)$ into which electrons are transferred when the relative energy separation between the two edges is lowered by pressure. The measured results are compared with calculations based on the model proposed by Ehrenreich. The agreement between theory and experiment is found to be good if certain parameters are varied in a systematic way. For lightly doped material the mobility ratio of electrons in the light mass band to those in the heavy mass band is found to be large and to decrease rapidly with increasing temperature. At higher carrier concentrations both the magnitude of the mobility ratio as well as its variation with temperature are substantially reduced. At 300°K the (000) and (100) minima are found to cross at $x\approx0.44$ if we assume Vegard's law to be valid. The experimental data are best explained if it is assumed that the separation between the two sets of minima changes at a rate of $>1\times10^{-4}$ eV/°K.

INTRODUCTION

In the last few years considerable progress has been made in the understanding of compound semiconductors, in particular those consisting of elements from the III–V columns in the periodic table. A comprehensive review of the transport properties of a number of these has been given by Ehrenreich,[1] who also deduced the band structure of Ga$(As_{1-x}P_x)$ as a function of the composition variable x. The details have been exhaustively covered by that author in an earlier publication[2] and therefore we shall only review those points of his model that are of direct concern to us here. Unlike the majority of semiconductors investigated to date, Ga$(As_{1-x}P_x)$ displays two sets of conduction band edges which are close enough in energy over an appreciable portion of the composition range so that their combined influence on the electrical behavior of the semiconductor has to be considered. The separation in energy between the two sets of minima depends upon x and it vanishes for $x\approx0.5$. For $x<0.5$ the (000) minimum is lowest in energy, while for $x>0.5$ the (100) valleys are believed to be lowest. Because of the large differences in the mobilities and density of states between them, the bulk properties of the material can be expected to change appreciably as the region $x=0.5$ is approached. It is the purpose of this paper to report measurements made in that transition region under the application of hydrostatic pressure and to derive values for parameters that so far have been speculative or not known at all. The influence of hydrostatic pressure on the band structure of semiconductors has been discussed by Paul.[3] He also touches upon some of the discrepancies in the experimental results in GaAs, which have a direct bearing on the model of both that compound and that of Ga$(As_{1-x}P_x)$ itself.

Our approach in this paper is to assume the correctness of the model proposed in Ref. 2. We hope to determine several band-structure parameters by fitting our results to this model. As will become apparent shortly, the biggest difficulties in accomplishing our task arise from the lack of homogeneity in the crystals themselves.

EXPERIMENTAL DETAILS

The Ga$(As_{1-x}P_x)$ samples used for the measurements were obtained from various sources. The most homogeneous samples were cut from crystals grown by halogen-assisted vapor transport in a sealed capsule somewhat similar to the method reported by Pizzarello.[4] Others were grown from excess gallium solution and one was an epitaxially grown sample purchased from the Merck Company. All crystals were doped with Te. X-ray determination of the lattice constant in conjunction with Vegard's law was used to establish the composition most accurately. All the crystals grown by vapor transport were prepared to yield $x\approx0.35$. Whenever possible the specimens were cut into rectangular bars about 10 mm long and 1 mm square. Ohmic contacts were made by alloying tin dots to the semiconductor. The pressure was generated in a cylindrical multiple wall pressure cell of conventional design.[5] The pressure generating piston was driven directly by the platen of a 50-ton press. At room temperature the measurements were carried out inside this cylinder, while at the other temperatures the samples were enclosed in a small pressure cell similar to the one reported by Fitchen.[6] The large pressure cylinder then was used as the pump and connected to the small cell by $\frac{1}{8}$-in. o.d., 0.024-in. i.d. hard-drawn stainless-steel tubing manufactured by the Harwood Engineering Company. The electrical connections were made by the use of

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[1] H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).
[2] H. Ehrenreich, Phys. Rev. **120**, 1951 (1960).
[3] W. Paul, J. Appl. Phys. **32**, 2082 (1961).
[4] F. A. Pizzarello, J. Electrochem. Soc. **109**, 226 (1962).
[5] C. A. Swenson in *Solid State Physics*, edited by F. Seitz and D. Turnbill (Academic Press Inc., New York, 1960), Vol. 11, p. 41; P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949).
[6] D. B. Fitchen, Rev. Sci. Instr. **34**, 673 (1963).

0.062-in. swaged metallic sheathed thermocouple wire.[7] At temperatures below 300°K a mixture of *n* pentane and isopentane served as the pressure fluid while at temperatures above that *n* pentane alone was used. The pressure was measured by a seasoned manganin wire gauge[5] mounted inside the pressure cylinder. The gauge calibration was established using a recent determination of the freezing pressure of Hg at 0°C.[8] The accuracy of the pressure measurements is estimated to be better than 1%.

RESULTS

The application of hydrostatic pressure on Ga$(\mathrm{As}_{1-x}\mathrm{P}_x)$ increases the energy gap between the conduction band minimum at $k=(000)$ and the top of the valence band at the rate of about 1.1×10^{-5} eV/atm. The energy separation between the (100) minima and the valence band has a small negative pressure coefficient and therefore the net result is a decrease of the relative energy separation ΔE between the (000) and (100) conduction band valleys under pressure. As long as $\Delta E \gg kT$ the number of electrons transferred to the energetically higher lying minima per unit dilatation of the crystal is small. Once ΔE has been reduced to a few kT either by very high pressures in the case of [2]GaAs or by the proper choice of composition in Ga(AsP), the rate of transfer of electrons to the higher valleys increases rapidly. Because of the much lower electron mobility in the (100) valleys, the bulk resistance of the material increases many fold until all the current is carried by electrons in the (100) valleys. After that a further increase in pressure does not change the resistance appreciably. This general characteristic is demonstrated by the measurements shown in Figs. 1, 3, and 4.

As mentioned already our plan is to compare experiment and theory by choosing certain parameters of Ehrenreich's model until a best fit with the measured values is obtained. With the assumptions set down in the Appendix we find for the relative resistance at pressure P

$$\frac{\rho(P)}{\rho(0)}=\frac{b+\nu}{1+\nu}\,\frac{1+\nu e^{\alpha P/kT}}{b+\nu e^{\alpha P/kT}}, \tag{A1}$$

where $b=\mu_1/\mu_2$ is the mobility ratio between valleys 1 and 2, $\nu=b_\rho e^{-\Delta E(0)/kT}=n_2(0)/n_1(0)$ the ratio of the number of electrons in valley 2 to the number in valley 1 at atmospheric pressure, and α the pressure coefficient of the energy separation between valleys 1 and 2. Valley 1 refers to the minimum at $k=(000)$ while 2 refers to the set of equivalent minima along $k=(100)$. In trying to fit Eq. (A1) to the experimental data, the value for the pressure coefficient α was accepted from earlier work. It was deduced directly from pressure measurements on [2]GaAs and probably can be accepted with some confidence.[9] Should a small correction for this value become necessary it would merely lead to a minor correction in b as seen by Eq. (A4) of the Appendix. The density of states ratio b_ρ is numerically quite uncertain[2] and may be subject to correction. Fortunately for most of our considerations b_ρ is absorbed into the factor ν and will only become important when the band structure at a particular value of x is discussed.

Figure 1 shows the results of measurements made on sample 21a-11, the crystal with the smallest carrier concentration of all our samples. This single-crystal specimen obtained from a crystal grown by vapor transport also had a small variance in composition and therefore we will base our conclusions largely on that particular sample. Other bars cut from adjacent parts of the same crystal gave results very close to 21a-11, so that our confidence seems justified. Except for the high-pressure region, i.e., the region after the bands have crossed, the fit is considered to be very good. The outstanding feature of the curves plotted in Fig. 1 is the behavior of $b=\mu_1/\mu_2$ as a function of temperature. It has a very large value at 200°K but decreases markedly as the temperature is increased. For the deviations between the expected and the actual measured values at

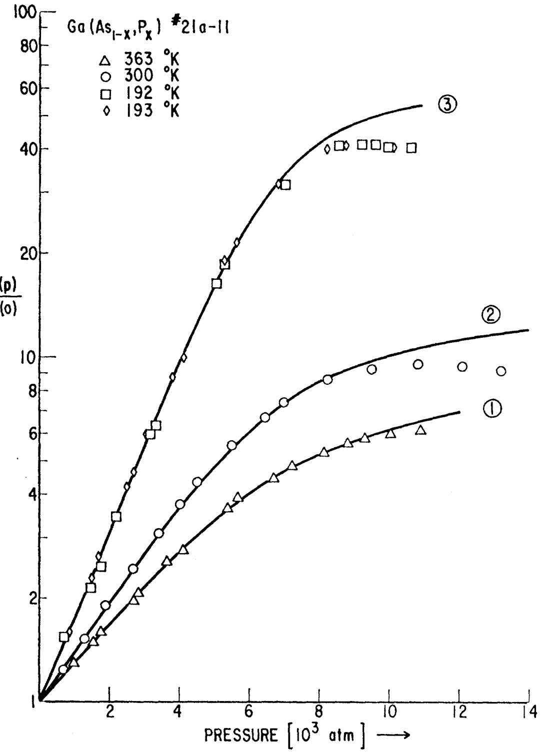

FIG. 1. Relative resistance versus pressure: Ga$(\mathrm{As}_{1-x}\mathrm{P}_x)$, No. 21 a-11, $x=0.359$. Curve 1: $\nu=7.2$, $b=55$; curve 2: $\nu=5.6$, $b=75$; curve 3: $\nu=4.8$, $b=320$.

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

[8] D. H. Newhall, L. H. Abbot, and R. A. Dunn, American Society of Mechanical Engineers, New York Meeting, 1962 (unpublished).

[9] For GaP this coefficient has been found to be larger by about 25%. See Ref. 3.

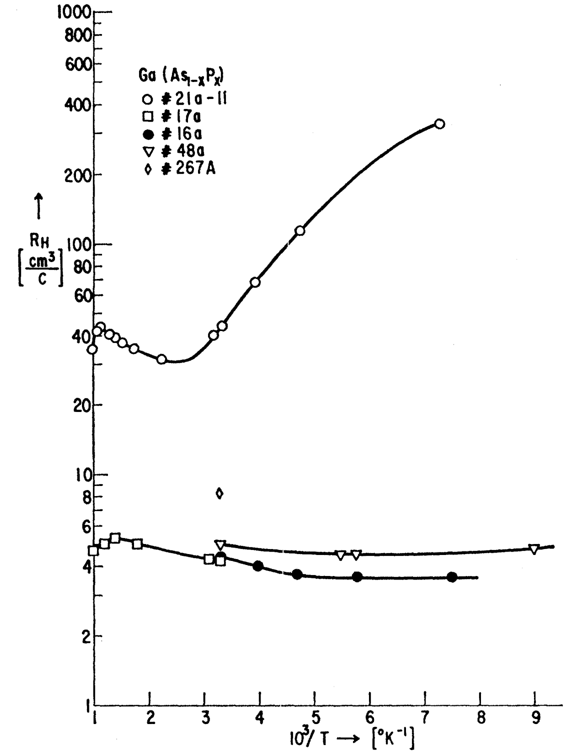

FIG. 2. Hall constant versus $1/T$ at atmospheric pressure.

high pressures, we offer the following explanation: The inspection of the Hall coefficient (Fig. 2) for this sample reveals that freeze out of carriers occurs below 400°K. This implies that an appreciable number of carriers is occupying one or more deep levels at the temperatures at which our experiments are performed. If we suppose that these levels have a pressure shift equal to that of the (000) minimum, then the number of electrons in that band will not change under pressure as long as the other minima are sufficiently far removed in energy. As the (000) minimum approaches the (100) minima, some of the carriers in the impurity levels can now be thermally excited into the (100) minima. Now our assumption that the total number of electrons in the conduction band remains constant is no longer valid. Because of the large mobility of electrons in the (000) minimum, this effect will not be noticeable until the latter valley is almost empty; i.e., until the bands have crossed. Then, as carriers are transferred from the bound impurity states to the low but finite mobility (100) band, the resistance decreases in agreement with the observations. The effect should become more pronounced as the temperature is decreased, because the ratio of electrons in the (000) minimum to the number in bound states is decreased even before the pressure is applied. For the samples that do not show the freeze out, this decrease in resistance does not occur, giving further support to the correctness of our reasoning.

Figure 3 shows the results of measurements made on sample 17a. This specimen is also a single crystal and are similar in composition to 21a-11. The major difference between the two crystals is the much larger carrier concentration of 17a. This difference shows up in the reduction of the mobility ratio b which can be traced to the increased influence of ionized impurity scattering in the heavier doped crystal. Because this scattering process is most important at low temperatures, it reduces the temperature dependence of b.

The results of measurements on additional samples are shown in Fig. 4. Specimen 48a is a polycrystalline sample which shows a pressure dependence similar to 17a. However, the factor ν which results in the best fit with the experimental data has a different temperature dependence for the two samples. It is probable that the polycrystalline sample 48a has a larger variation in composition which would explain the different behavior. A very pronounced effect of this variation can be seen in sample 267 A with $x=0.24\pm0.05$. This epitaxially grown single crystal shows such large variations in composition that no agreement between our model and experiment can be accomplished.

Finally, we have measured a sample with a composition of $x\approx0.61$ and find the change in resistance linear up to 10 000 atm at room temperature with $\Delta\rho/(\rho P)=-14.5\pm1\times10^{-6}$ atm^{-1}. This agrees in sign with the

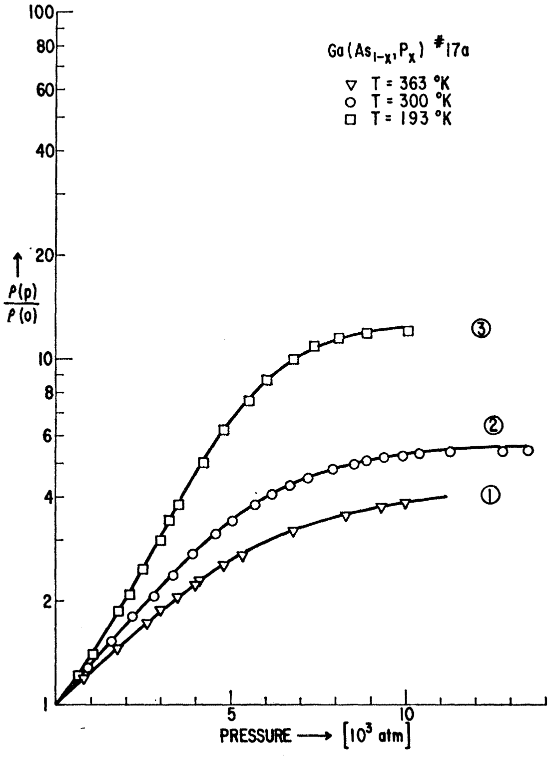

FIG. 3. Relative resistance versus pressure: $Ga(As_{1-x}P)$, No. 17a, $x=0.372$. Curve 1: $\nu=5.3$, $b=22$; curve 2: $\nu=3.3$, $b=22$; curve 3: $\nu=0.85$, $b=23$.

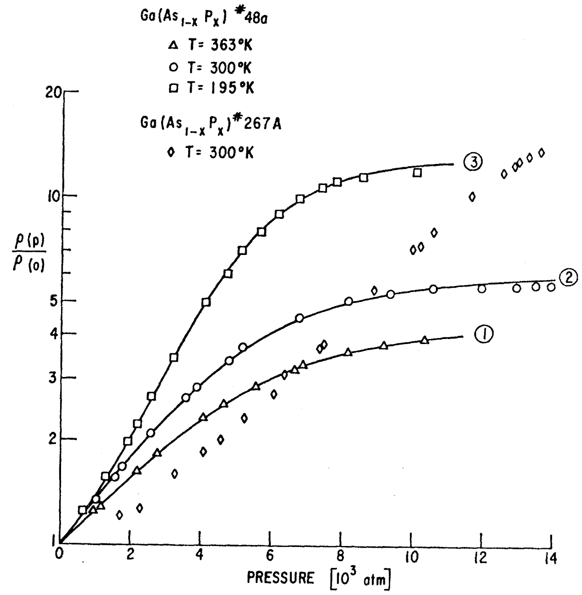

FIG. 4. Relative resistance versus pressure: Ga(As$_{1-x}$P) No. 48a, $x=0.367$, and No. 267*A*, $x=0.24$. Curve 1: $\nu=6.1$, $b=25$; curve 2: $\nu=4$, $b=26$; curve 3: $\nu=0.85$, $b=23$.

measurements made on[10] silicon and[11] GaP, but is larger in magnitude than either one of these.

We shall now attempt to gain additional information from the measurements made on sample 21a-11. From the pressure data we find $\nu=5.6\pm1$. (See Table I.) If we accept the value of $b_\rho=70(+40, -20)$ determined by Ehrenreich,[2] we find the energy separation between valleys 1 and 2 at zero pressure given by $\Delta E(0)=0.065$ eV ($+0.017$, -0.013). X-ray lattice-parameter evaluation resulted in a value of $a_0=5.5806\pm0.0002$ or, assuming the validity of Vegard's law, $x=0.359$. Linear extrapolation of our energy separation ΔE to the terminal compounds GaAs and GaP shows that we cannot match both values given in Ref. 2 simultaneously. The pressure data of Howard and Paul[12] rule against an energy separation between the direct and indirect band edges in GaAs of less than 0.3 eV. Ehrenreich found 0.36 eV as the most consistent value based on Hall and pressure measurements. In Fig. 5 we have plotted the energy separation ΔE as deduced from our measurements. If we accept 0.36 eV as the energy separation between the (000) and (100) minima for GaAs, the separation for GaP turns out to be 0.46 eV if we assume a linear dependence of ΔE on x. This is 0.1 eV larger than reported earlier.[1] From an analysis of optical absorption and reflectivity data Zallen and Paul[13] find 2.75–2.8 eV for the direct gap energy in GaP. With a value of about 2.2 eV for the indirect gap energy E_G this leads to an energy separation ΔE of about -0.5 to -0.6 eV. Photothreshold measurements by Spitzer and Mead[14] indicate that $\Delta E\approx-0.45$ eV. Engeler,[15] of this laboratory, concludes that a value of 0.5 eV for the separation of the (100) and (000) band is consistent with Spitzer and co-workers'[16] optical absorption data. Figure 5 indicates the two sets of minima to cross in energy at $x_c\approx0.44$, somewhat smaller than the earlier deduced value of $x_c\approx0.53$. The assumption that ΔE depends linearly on x is undoubtedly only an approximation, but the deviations are not expected to be large enough to affect our determination of x_c materially.

TABLE I. Experimentally determined values of ν and b as function of temperature for several samples. α_0=lattice parameter from x-ray measurements. Composition parameter x deduced from α_0 assuming validity of Vegard's law. $\Delta E(0)$ is nominal value based on $b_\rho=70$.

Sample No.	α_0 [Å]	x	T [°K]	ν	$\Delta E(0)$ [eV]	$b=\mu_1/\mu_2$
21a-11	5.5806	0.359	193	4.4 ±1	0.045	300±50
	±0.0002		300	5.6 ±1	0.065	75±15
			363	7.2 ±1.2	0.075	55±15
17a	5.5780	0.372	193	0.85±0.2	0.073	23±3
	±0.0001		300	3.3 ±1	0.079	22±3
			363	5±1	0.087	21±3
48a	5.5789	0.367	193	0.85±0.2	0.073	23±3
	±0.0001		300	4±1	0.074	26±5
			363	6.1 ±1.1	0.08	25±4
NH 1 No. 4	5.5738	0.39	300	10±2	0.05	30±7
	±0.0004					

The main difficulties in the interpretation of our results show up when we try to determine the effect temperature has on the energy separation ΔE. Again accepting the value $b_\rho=70$ independent of temperature, we can find ΔE from ν. This is done in Table I for three samples discussed earlier. In order to arrive at the probable error of these determinations, curves calculated by varying both b and ν were compared with the actual measurements. The limit of agreement was defined as that point at which the deviations of the calculated curves from the measured have passed outside the experimental tolerances. The discrepancies in the temperature coefficient of ΔE for the three samples are larger than the experimental error. In view of the difficulties arising from crystal inhomogeneities, as exemplied by results from sample 267 A, this is not too surprising. It must be concluded, though, that $\partial\Delta E/\partial T = (\partial/\partial T)(E_{100}-E_{000})$ is larger than 1×10^{-4} eV/°K.

While the changes of resistance under pressure can readily be understood in terms of the adopted model, the interpretation of the Hall data derived from the same samples is not at all certain. The Hall coefficient for the two-band model is given by

$$R_H=[(1+\nu)/en][(b^2+\nu)/(b+\nu)^2],$$

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[10] C. S. Smith, Phys. Rev. **94**, 42 (1954).

[11] A. Sagar and R. C. Miller, J. Appl. Phys. **32**, 2073 (1961).

[12] W. E. Howard and W. Paul, quoted in Ref. 3.

[13] R. Zallen and W. Paul (to be published).

[14] W. G. Spitzer and C. A. Mead (to be published).

[15] W. E. Engeler (private communication).

[16] W. G. Spitzer, M. Gershenzon, C. J. Frosh, and D. F. Gibbs, Phys. Chem. Solids **11**, 339 (1959).

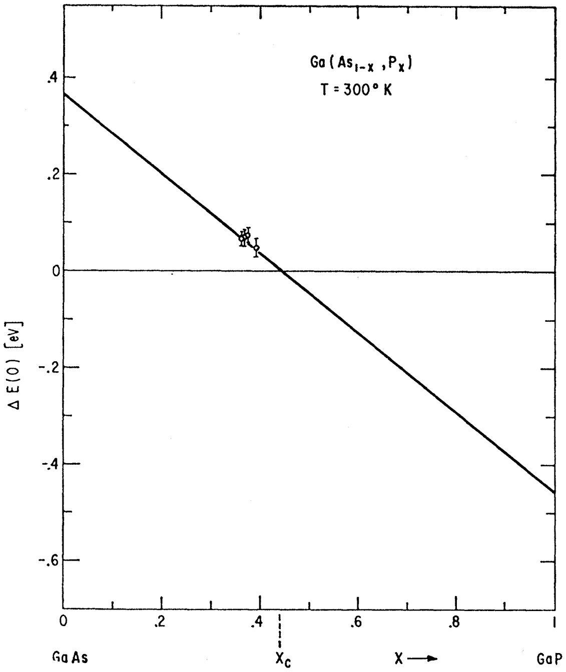

FIG. 5. Energy separation $\Delta E(0)$ versus composition at atmospheric pressure and 300°K. The uncertainty in the experimental points is due to the experimental errors as well as the large uncertainty in the knowledge of b_p.

where scattering factors of the order of 1 have been set equal to 1. Under the condition $n_1+n_2=n=$ constant, R_H has a maximum value of $(1+b)^2/4b$ when $n_2/n_1=b$. The temperature at which this maximum occurs increases with b and ΔE. To be consistent with the parameters deduced from the pressure experiments, the Hall coefficient should have increased appreciably at room temperature over its value at lower temperatures assuming ΔE to be temperature-independent. This, however, is contrary to the experimental evidence. Furthermore, the maximum of R_H occurs at much higher temperatures than expected from the energy separation of the (000) and (100) valleys at room temperature.

For the lightly doped sample 21a-11, the rapid freeze out below 400°K invalidates our assumption that the total number of electrons in the conduction band remains constant. This fact and the rapid decrease of b with increasing temperature could be advanced as a reason for the poor agreement with the measured Hall coefficient. Both arguments are not supported by the measurements made on the rest of the samples and, therefore, we are forced to look for other possible explanations. As mentioned earlier, the pressure measurements at various temperatures are best explained if we assume ΔE to have a positive temperature coefficient in excess of 1×10^{-4} eV/°K. An increase of the energy separation ΔE at a rate of about 2×10^{-4} eV/°K and a decreasing b would suffice to keep R_H approximately constant to higher temperatures, except that this is contrary to the experience with the other group IV and III–V semiconductors as well as the terminal compounds themselves. It should be noted, however, that very little is known about transport properties of ternary compounds and some of the extrapolations might well be in error.

CONCLUSIONS

The close agreement between the measured values and the calculations based on Ehrenreich's model of the Ga$(As_{1-x}P)$ conduction band must be considered strong evidence for the correctness of the essential points of that model. While we have not directly proved that the energetically higher lying minima are indeed along the ⟨100⟩ directions, the self-consistency of our results gives strong support to this identification.

The large mobility ratio $(b>50)$ deduced from our room temperature measurements on the lightly doped sample is significant, since this is necessary for the interpretation of the large pressure-dependent resistance changes in GaAs observed by Howard and Paul.[12] The rapid decrease of the mobility ratio b with increasing temperature could explain the smallness of b derived from high-temperature Hall data. Extended to GaAs, it suggests that this is the reason for the apparent difference in $b=10$ reported by Aukerman and Willardson[17] and the b based on room-temperature pressure measurements. But in view of the discrepancies between our pressure and Hall data, this interpretation must be considered with caution. The composition x_c at which the (000) and (100) minima are equal in energy is smaller than earlier estimates, excepting the recent determination of Spitzer and Mead.[14] The extrapolation of their results to GaAs leads to an energy separation which is too small. Their results can be brought into agreement with ours if we assume some variation in composition in their samples. This variation would have the effect of lowering the apparent energy of the (100) band edge for a given value of x explaining the difference in their results.

ACKNOWLEDGMENTS

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APPENDIX

We are assuming that the conduction band of Ga(As,P) exhibits two sets of minima, one minimum at

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[17] L. W. Aukerman and R. K. Willardson, J. Appl. Phys. **31**, 939 (1960).

$k=[000]$ (valley 1) and a set of minima along $k=[100]$ in the Brillouin zone (valley 2). The separation in energy between the minima at the different points in the Brillouin zone is supposed to be a linear function of the composition of the alloy as shown in Fig. 5. For the purpose of the analysis we make these further simplifying assumptions:

1. Boltzman statistics apply.
2. Intervalley scattering is neglected.
3. The total number of carriers in the conduction band is constant.
4. The mobility ratio $b=\mu_1/\mu_2$ is independent of pressure. (Subscript 1 refers to the low-mass band at $k=[000]$ throughout this analysis. Furthermore, symbols used are those of Ehrenreich.[2])
5. $b_p=(m_p/m_1)^{3/2}=70$ is also pressure- and temperature-independent; m_p= density of state mass in the valleys at $k=[100]$.
6. The energy separation between different minima is $\Delta E=\Delta E(0)-\alpha P$ where $\alpha=1.1\times10^{-5}$ eV/atm.

With these assumptions we find for the relative resistance at pressure P,

$$\frac{\rho(p)}{\rho(0)}=\frac{b+\nu}{1+\nu}\,\frac{1+\nu e^{\alpha P/kT}}{b+\nu e^{\alpha P/kT}}, \tag{A1}$$

where

$$\nu=\frac{n_2(0)}{n_1(0)}=\left(\frac{m_p{}^{3/2}}{m_1}\right)e^{-\Delta E(0)/kT}.$$

The logarithmic derivative of the expression (A1) is given by

$$\frac{d\ln\rho}{dP}=\left(1-\frac{1}{b}\right)\frac{\alpha}{kT}\,\frac{\nu e^{\alpha P/kT}}{[1+(\nu/b)e^{\alpha P/kT}](1+\nu e^{\alpha P/kT})}. \tag{A2}$$

Since ν can directly be converted into composition by the use of Fig. 5, this last equation gives essentially a universal curve in which composition and pressure can be interchanged. In principle, it should therefore be possible to plot the experimental values of the logarithm of resistance versus pressure, differentiate this curve and fit the resulting curve to (A2). Attempts to accomplish that in general were not satisfactory, primarily because b was different in every crystal and the graphical differentiation lacked accuracy.

Specific values of (A1) and (A2), however, are useful in finding the unknown parameters ν and b.

For the limit of high pressures, we get from (A1)

$$\lim_{P\to\infty}\frac{\rho(P)}{\rho(0)}=\frac{b+\nu}{\nu+1}, \tag{A3}$$

and for the maximum value of (A2) we find

$$\left.\frac{d\ln\rho}{dP}\right|_{\max}=\frac{\alpha}{kT}\,\frac{1-1/b}{1+2/\sqrt{b}}. \tag{A4}$$

The influence of assumptions 4 and 5 on the result (A1) can be judged if we let

$$\frac{\mu_1(P)}{\mu_1(0)}=\left(\frac{m_1(0)}{m_1(P)}\right)^n. \tag{A5}$$

From Ref. 2,

$$\frac{m_1(P)}{m_1(0)}=\frac{E_G(P)}{E_G(0)}\,\frac{1+(1/2)E_G(0)[E_G(0)+\Delta]^{-1}}{1+(1/2)E_0(P)[E_G(P)+\Delta]^{-1}}, \tag{A6}$$

where $E_G(0)$ and $E_G(P)$ are the band-gap energy at atmospheric pressure and at pressure P respectively and Δ the spin-orbit splitting energy. If polar scattering is the dominant scattering mechanism, n in equation (A5) equals $\frac{3}{2}$ and (A1) can be corrected by replacing the one in the numerator by the right hand side of (A6) raised to the $\frac{3}{2}$ power. Since $\Delta\ll E_G$ (A6) is approximately

$$1+\frac{1}{E_G(0)}\left(\frac{\partial E_G}{\partial P}\right)P.$$

This factor has to be considered only for values of ν and P where the electron transfer to the higher band edge is insignificant.