

Pressure and compositional dependences of the Hall coefficient in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and their significance

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(Received 8 June 1979)

The Hall coefficients have been measured in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of hydrostatic pressure, temperature, and the compositional parameter x , and are shown to consist of two contributions. These result from (1) the electron distribution in the Γ , L , and X conduction-band minima and (2) the freeze out of electrons to the donor levels due to an increase in the donor ionization energy with pressure or Al concentration. We have analyzed the experimental data for R_H in terms of the three-band model to separate out these contributions and have shown that R_H representing purely contribution (1) goes through a maximum near the Γ - X crossover pressure. The donor ionization energy rises from 6 to 101 meV under hydrostatic pressure in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$. As a function of composition the ionization energy increases from 6 to 101 meV with a peak at 130 meV near the composition $x = 0.45$ at which a crossover from the direct to the indirect energy gap occurs. From these results it is shown that the donor levels attached to the Γ , L , and X minima are 6, 150, and 101 meV below the respective minima. The variation of the Hall coefficient, the mobility, and the donor ionization energy with composition or pressure are shown to be consistent with the direct-indirect crossover effect.

I. INTRODUCTION

The ternary semiconducting $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compounds have been extensively studied in recent years because of their potential for a wide variety of technological applications. With the substitution of Al into the Ga sublattice, all the three conduction-band minima, namely, Γ , L , and X , move to higher energies. Of these, the direct minimum Γ which is the lowest in GaAs moves at a faster rate with x than L and X , and at $x = 0.45$ crosses the X band.¹ Consequently at higher Al concentrations the X band becomes the lowest conduction band. Because of this shift in the conduction-band type, the electrical and optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ strongly depend on the Al content.

Springthorpe *et al.*² performed Hall measurements on n -type Te-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ over a wide range of composition and obtained the ionization energies of the donor directly from the temperature dependence of the Hall coefficient R_H . They reported that the ionization energy for the Te donor went through a maximum with composition and attributed this to an increase in the ionization energy at the crossover composition. However, they neglected an important contribution to the Hall coefficient R_H . In the crossover region the conduction electrons are distributed among all three conduction-band minima Γ , L , and X which have widely different mobilities and effective masses. In this circumstance R_H is no longer simply equal to $1/ne$, but rather is a complicated

function of the mobilities and the electron concentrations in the three bands, as well as of temperature.

It is a well-established fact that the application of hydrostatic pressure causes both the Γ and L conduction-band minima to move to higher energies and the X minima to move very slightly to lower energies. Therefore, it occurred to us that the different contributions to R_H can be conveniently sorted out, by using high pressure as a tool to vary the positions of the conduction-band minima in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compounds. With samples having different Al content the Γ - X crossover can be made to occur in the 0–35-kbars range and the system studied in the Γ , Γ - X crossover, and X -band regimes. Further, the effect can be studied without changing such parameters as doping or compensation, hence facilitating the interpretation of the data.

In the present study we have measured the Hall coefficient and resistivity of a number of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compounds as a function of temperature at different pressures, as well as a function of pressure up to 40 kbars at room temperature. The normalized Hall coefficient when plotted against pressure exhibits a maximum at a pressure depending upon the Al concentration. The resistivity rises rapidly in the carrier transfer region and saturates at high pressure. The Hall coefficient versus $1/T$ curves at different pressures have been analyzed in terms of the three-band model. The effect of electron distribution

among the three minima was separated from the freeze-out of electrons into the donor levels. Hall data obtained as a function of composition have again been analyzed and were compared with the results obtained under pressure.

II. EXPERIMENTAL PROCEDURE

The n -type Sn-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers were grown by the method of liquid-phase epitaxy on (100)-Cr-doped semi-insulating GaAs substrates. The substrates were baked in an H_2 atmosphere for 16 h at 800°C . A conducting surface layer is always formed during the baking treatment.³ This must be removed before growing the epilayer, otherwise the surface layer would conduct in parallel with the epitaxially grown layer, resulting in ambiguous Hall data. To remove this layer, the GaAs seed was melt etched just prior to layer growth. When the temperature of the growth boat was being raised to the growth temperature (850°C), the heating was interrupted at 825°C , and the substrate was inserted under the growth melt. Then, as the temperature was raised to the growth temperature, about $30\ \mu\text{m}$ of the substrate was dissolved into the growth melt. The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layer was grown by cooling the boat from 850°C at a cooling rate of $0.2^\circ\text{C}/\text{min}$. The thickness of the grown layers was typically between 8 to $15\ \mu\text{m}$. The exact compositions of the samples were determined by photoluminescence for $x < 0.35$ and from low-temperature absorption combined with the Auger sputtering technique for $x > 0.35$.¹

Clover-shaped samples were cut ultrasonically to Van der Pauw geometry. In the case of samples used in Hall measurements at atmospheric pressure, Ohmic contacts were obtained by spark alloying $50\text{-}\mu\text{m}$ Au-2-wt.-%-Sn wires to the edges of the samples. For samples used in pressure studies, the contacts were formed by evaporation of Au and Sn and subsequent heating to 400°C in hydrogen. Copper wires were cold welded to the contacts using indium, before connecting the sample to the pressure cell leads.

For generating the required hydrostatic pressure a piston-cylinder device was employed, with a Teflon cell to contain the pressure medium.⁴ For Hall measurements we used the technique that has been described in a recent publication.⁵ In this technique a copper coil is placed inside the Teflon cell to generate the magnetic field; with a current of $3\ \text{A}$ a field of $210\ \text{G}$ was obtained inside the coil. The sample was located in the middle section of the coil, where the magnetic field was uniform. The unbalanced voltage between Hall contacts for zero magnetic field due

to the asymmetrical position of the contacts was compensated using a potentiometer and a battery. For monitoring the temperature a copper-Constantan thermocouple junction was placed close to the sample.

For obtaining low temperatures at high pressure, the pressure vessel assembly was cooled by circulating liquid nitrogen through a well formed on top of the vessel. The pressure vessel assembly was thermally isolated from the press frame by introducing 10-mm thick Transite discs between the press platons and the top and bottom end-loading plates. With this arrangement it was possible to reach temperatures as low as 150°K . Pressure was always applied at room temperature and then the cooling sequence was initiated. During cooling the gauge pressure dropped and hence the cooling cycle was found to be inappropriate for taking data. Therefore Hall data were taken during the warming cycle, when it was possible to keep the gauge pressure constant by bleeding the excess pressure, which results from the temperature rise. It is to be noted in this connection that pressure should never be applied when the pressure medium is frozen, since then the sample would be subjected to nonhydrostatic stresses. It is known,⁶ however, that the pressure distribution remains hydrostatic if the medium is frozen after the pressure has been applied.

III. RESULTS OF HALL MEASUREMENTS UNDER HYDROSTATIC PRESSURE

In Fig. 1 the Hall coefficient normalized to its value at atmospheric pressure $R_H(P)/R_{H0}$ is plotted as a function of pressure for a number of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples, as well as for GaAs ($x=0$), all at room temperature. In Fig. 2 the normalized Hall coefficient is presented as a function

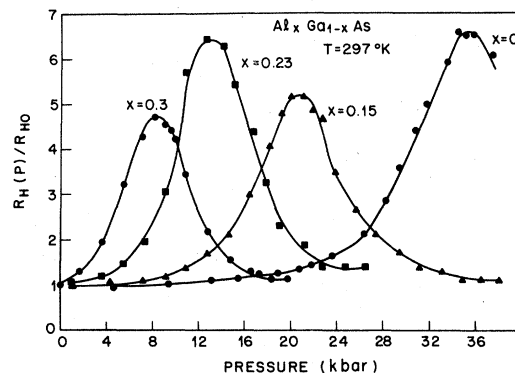


FIG. 1. The measured Hall coefficient (normalized to the value at atmospheric pressure) plotted as a function of pressure for some $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples.

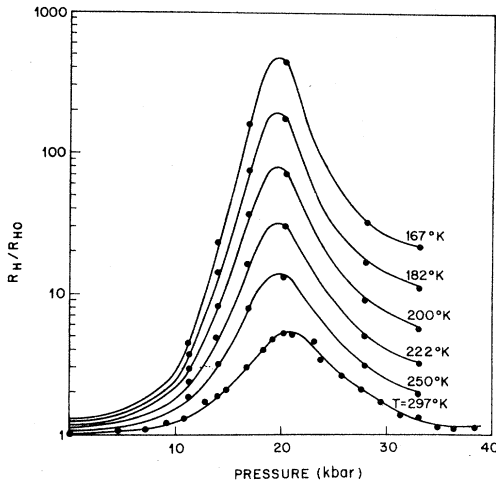


FIG. 2. The measured Hall coefficient (normalized to the value at atmospheric pressure and $T=297^\circ\text{K}$) as a function of pressure at different temperatures for $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$.

of pressure at different temperatures for the sample $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$. The data for the plot in Fig. 2 were obtained from experiments in which pressures were held constant and the temperature was varied. The experimental data shown in Fig. 3 represent R_H/R_{H0} versus $1/T$ at different pressures for the same sample.

The important feature of the data in Fig. 1 is that the Hall coefficient curves have a maximum

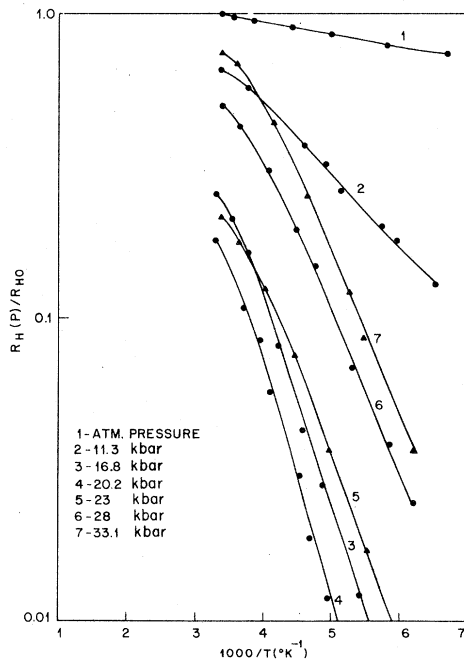


FIG. 3. Experimentally obtained normalized Hall data plotted as a function of $1/T$ at different pressures.

which occurs at pressures specific for each compound. For GaAs we observe the maximum at 35.5 kbars. Pitt and Lees⁷ have reported that the maximum occurs for GaAs at 33 kbars. The difference is probably due to the presence of some nonhydrostatic component in the pressure distribution in the opposed anvil device they used.

The Hall curves presented in Fig. 2 exhibit a maximum which remains more or less at the same pressure as the temperature is varied. However, the most interesting aspect of the data is that the normalized Hall coefficient does not reach unity at high pressure, the effect being more pronounced at lower temperatures. The reason for this behavior is that the number of electrons is not constant throughout the pressure range because of the carrier freeze-out, due to an increase in the donor ionization energy with increasing pressure. We shall return to this point in Sec. IV.

IV. DISCUSSION OF HALL MEASUREMENTS UNDER HYDROSTATIC PRESSURE

A. Analysis of Hall data

Since the electron distribution involves all three conduction-band minima (Γ , L , and X) in our pressure and compositional range, we will analyze the Hall data using a model involving all three conduction-band minima with one donor level attached to each minimum. The Hall coefficient R_H in such a model is⁸:

$$R_H = \frac{1}{en} \frac{\alpha_\Gamma + (\mu_{HL}/\mu_{H\Gamma})^2 \alpha_L + (\mu_{HX}/\mu_{H\Gamma})^2 \alpha_X}{[\alpha_\Gamma + (\mu_{HL}/\mu_{H\Gamma}) \alpha_L + (\mu_{HX}/\mu_{H\Gamma}) \alpha_X]^2} = \frac{1}{en} R_H^* \quad (1)$$

Here, $\alpha_i = n_i/n$ is the fraction of the total number of electrons in a particular minimum and μ_{Hi} is the Hall mobility in this minimum. Expression (1) indicates that if more than one minimum is populated the electron concentration, n is not simply equal to $1/R_H e$, but rather to $R_H^*/R_H e$.

R_H^* defined by (1) is a function of electron concentration in the three minima and their respective mobilities. Since the density of electrons in each conduction band depends on the relative position of the bands and the temperature, R_H^* is also a function of pressure P , composition x , and temperature T . A further complication arises from the fact that the total number of electrons n is not constant over the pressure range because the donor ionization energy strikingly changes with pressure and composition. Our purpose is therefore to separate out the above two contributions to R_H in the experimental data, namely, the contribution arising from electron distribution among the three minima and the effect of carrier

freeze-out due to the increasing donor ionization energy.

In expression (1) the α_i 's can be obtained using Fermi statistics. To calculate the Fermi level, we have used an approximation derived in Ref. 9. However, it should be borne in mind that the effective density of states mass of electrons used in the calculations is also a function of the position of the minima E_Γ , E_L , and E_X and of temperature. For nondegenerate statistics

$$M^* = \left[M_\Gamma^{3/2} + M_L^{3/2} \exp\left(\frac{E_\Gamma - E_L}{kT}\right) + M_X^{3/2} \exp\left(\frac{E_\Gamma - E_X}{kT}\right) \right]^{2/3}$$

in the direct region and

$$M^* = \left[M_\Gamma^{3/2} \exp\left(\frac{E_X - E_\Gamma}{kT}\right) + M_L^{3/2} \exp\left(\frac{E_X - E_L}{kT}\right) + M_X^{3/2} \right]^{2/3} \quad (2)$$

in the indirect region. Here M_Γ , M_L , and M_X are the effective masses of electrons in the Γ , L , and X minima, respectively.

Calculation of mobilities entering expression (1) is not an easy task. For the range of temperature in which we are interested, polar scattering is the dominant lattice scattering mechanism. In compensated samples, scattering due to ionized impurities is also important. Substitution of Al in the lattice introduces disorder scattering. In the direct-indirect gap transition region, nonequivalent valley scattering should also be considered, and in the indirect region intervalley scattering appears.^{10,11} Because of these complications we will use in our calculations the experimentally obtained Hall mobilities.

B. Behavior of $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$

In Fig. 4 we show the relative position of Γ ,

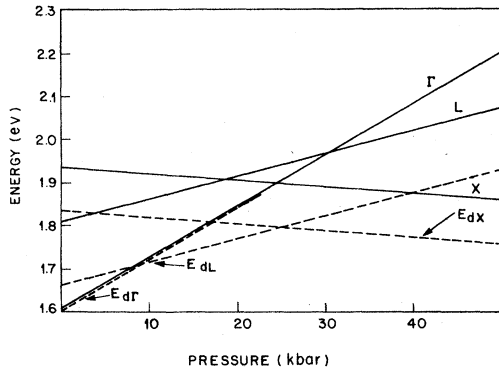


FIG. 4. The pressure dependence of Γ , L , and X band energies in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$. The Sn donor levels attached to the minima are also shown by dashed lines.

TABLE I. Values of parameters of $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ band structure and their pressure dependences.

$E_{s\Gamma}(P) = 1.61 + 0.0118P$ eV (Ref. 12)
$E_{sL}(P) = 1.81 + 0.0055P$ eV
$E_{sX}(P) = 1.935 - 0.0015P$ eV
$M_\Gamma(P) = \left[1 + 7.51 \left(\frac{2}{E_\Gamma(P)} + \frac{1}{E_\Gamma(P) + 0.341} \right)^{-1} M_0 \right]$ (Ref. 8)
$M_L^s(P) = 0.57 M_0$ (Ref. 15)
$M_X(P) = 0.84 M_0$ (Ref. 15)

^a Here M_L and M_X are effective density of states masses calculated as $M = \gamma^{2/3} (M_e M_t)^{1/3}$, where γ is a number of equivalent valleys.

L , and X minima in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ as a function of hydrostatic pressure (solid line). It is evident that the direct-indirect crossover occurs near 24.5 kbars at this composition. We chose this composition for a detailed study because the Γ - X crossover occurs at a convenient pressure; at the same time the carriers are entirely in the Γ and X bands at the low- and high-pressure ends, respectively. In our analysis of the data we will assume that all three conduction-band minima move with the same rate when the temperature is varied, so that the relative positions of the minima and the crossover pressure are not affected by temperature changes in the range of interest.

In Table I the parameters for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ used in our calculations and their sources are given. The calculated α_i 's are shown in Fig. 5 for $T = 297^\circ\text{K}$ and $T = 167^\circ\text{K}$. It can be seen that the L band lying approximately 60 meV above the crossover energy holds, at the most, 25% of the electrons at room temperature. At lower temperatures, when the electrons tend to populate the lower bands, the L band is even less populated. The figure also illustrates the transfer of electrons from Γ to X near the crossover.

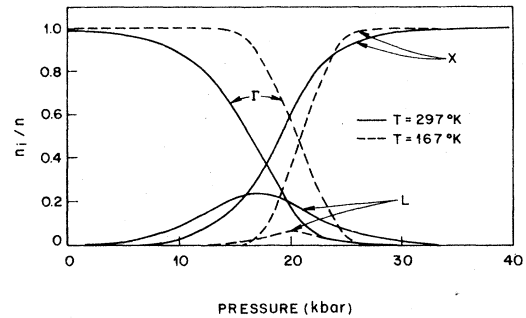


FIG. 5. Fractional electron concentration in the Γ , L , and X minima as a function of pressure in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ calculated using the model described in the text.

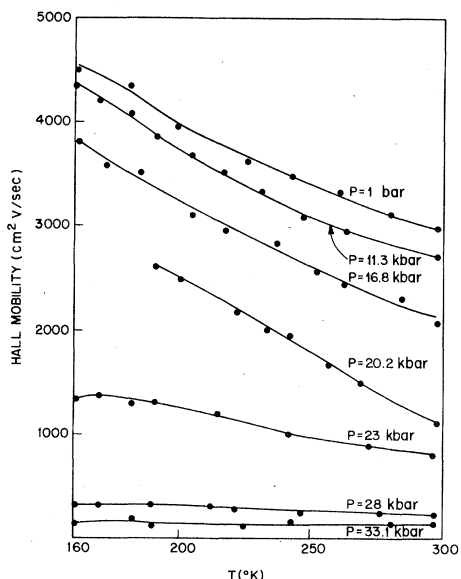


FIG. 6. The temperature dependence of the electron mobility in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ at different pressures.

In Fig. 6 we show the experimental Hall mobilities for $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ as a function of temperature at different pressures. Figure 7 shows the experimentally measured mobility (normalized to its value at atmospheric pressure) as a function of pressure at $T=297^\circ\text{K}$. The latter is a good illustration of the electron transfer from the Γ to the X band; the mobility changes from 3000 to $120 \text{ cm}^2/\text{V sec}$.

At atmospheric pressure all the electrons are in the Γ minimum and hence the upper curve of Fig. 6 represents the temperature dependence of the mobility in the Γ minimum. At pressures much higher than the crossover pressure, all electrons are in the X minima and the mobility reaches $120 \text{ cm}^2/\text{V sec}$. The bottom curve in Fig. 6 depicting μ_H as a function of temperature at $P=33.1 \text{ kbars}$ exhibits a very weak dependence on T . Hence we used the value of $120 \text{ cm}^2/\text{V sec}$ for $\mu_{H\Gamma}$ in our calculations.

Since it is not possible to separate out the L electron mobilities in our present study we are constrained to use the result obtained on GaSb.¹³ It has been shown that the L minima in GaSb is the lowest in the pressure range 10 to 25 kbars and the mobility ratio $\mu_L/\mu_\Gamma = 1/7.5$ at room temperature. Using this result we assign $\mu_{HL} = 3000/7.5 = 400 \text{ cm}^2/\text{V sec}$ at room temperature in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and assume that this value does not change substantially in the temperature and pressure range of our interest.

With all the parameters entering expression (1) available, we are in a position to calculate R_H^* at

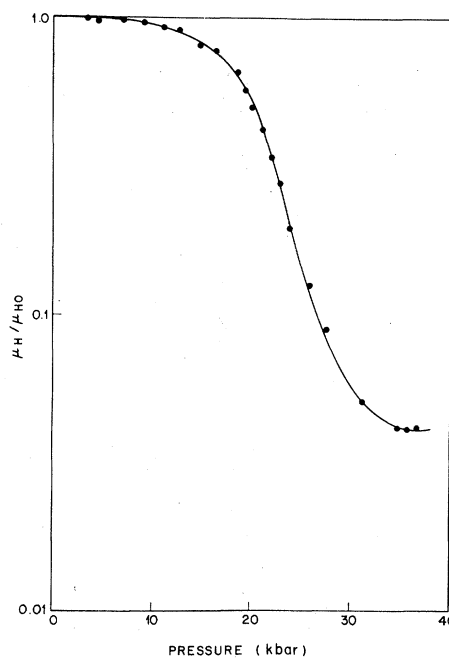


FIG. 7. The pressure dependence of the electron mobility in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ at 297°K .

any pressure or temperature. The results of such a calculation are shown in Fig. 8, where the calculated R_H^* is plotted as a function of pressure for $T=297^\circ\text{K}$ and 167°K .

It is evident that the shape of the low-temperature curve is narrower and has a higher value at the maximum. This can be explained by the fact that at low temperatures carrier transfer occurs within a narrower pressure range (see Fig. 5). The reason for the higher value at the maximum is that the ratio of $\mu_{H\Gamma}/\mu_{HX}$ at low temperatures increases and, in addition, the contribution of L electrons with intermediate mobilities becomes negligible.

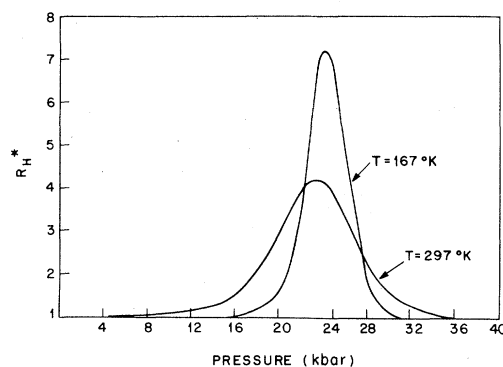


FIG. 8. The coefficient R_H^* in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ as a function of pressure calculated as described in the text.

We can now separate the freeze-out effect from R_H^* in the Hall data in Fig. 3. For each experimental point in Fig. 3, the ratios $R_H^*(T,P)/R_H^*(297^\circ\text{K},P)$ were calculated and the slopes of the curves were adjusted accordingly. After this

procedure the data represent only the pure freeze-out effect.

To extract ionization energies from the data, we use the following expression for carrier concentration¹⁴:

$$n = \frac{2(N_D - N_A)}{1 + (N_A/\beta N_c) \exp(E_d/kT) + \left\{ \left[1 + (N_A/\beta N_c) \exp(E_d/kT) \right]^2 + (4/\beta N_c)(N_D - N_A) \exp(E_d/kT) \right\}^{1/2}}. \quad (3)$$

Here N_D and N_A are donor and acceptor concentrations, parameters independent of pressure, N_c is the effective density of states which is dependent on temperature and pressure, β is the impurity-level spin degeneracy equal to $\frac{1}{2}$ for a donor. The ratio of electron concentration at pressure P to the electron concentration at atmospheric pressure then can be written as

$$\frac{n(P)}{n_0} = \frac{1 + \frac{N_A}{\beta N_{c0}} \exp\left(\frac{E_{d0}}{kT}\right) + \left\{ \left[1 + \frac{N_A}{\beta N_{c0}} \exp\left(\frac{E_{d0}}{kT}\right) \right]^2 + \frac{4}{\beta N_{c0}} (N_D - N_A) \exp\left(\frac{E_{d0}}{kT}\right) \right\}^{1/2}}{1 + \frac{N_A}{\beta N_c(P)} \exp\left(\frac{E_d(P)}{kT}\right) + \left\{ \left[1 + \frac{N_A}{\beta N_c(P)} \exp\left(\frac{E_d(P)}{kT}\right) \right]^2 + \frac{4}{\beta N_c(P)} (N_D - N_A) \exp\left(\frac{E_d(P)}{kT}\right) \right\}^{1/2}}. \quad (4)$$

We use at this point the fact that for two extreme cases—when all electrons are concentrated either in Γ or in X minima—the values of E_d can be found independently. From Hall measurements at atmospheric pressure (curve 1 in Fig. 3), E_d in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ was found to be 6 MeV. From Hall measurements on $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ (later in this study), the ionization energy of the Sn donor level associated with the minima was found to be 101 MeV. Further, $N_D - N_A$ has been obtained as $1.4 \times 10^{16} \text{ cm}^{-3}$ from Hall measurements at elevated temperature and atmospheric pressure. From the Hall coefficient as a function of pressure at 297°K, the value of $n(P=40 \text{ kbars})/n_0$ is equal to 1.134 (see Figs. 1 or 2). Knowing these values we are able to find N_A by using it as a fitting parameter in expression (4). We obtained $N_A = 7 \times 10^{16} \text{ cm}^{-3}$ which gives $N_D = 8.4 \times 10^{16} \text{ cm}^{-3}$, by fitting the data at atmospheric pressure and 40 kbars.

Having found N_D and N_A we can now fit the experimental freeze-out data to obtain E_d as a function of pressure. The result of this fitting is shown in Fig. 9. Each point represents the ionization energy at a given pressure, obtained by fitting the data according to expression (4), in this case using E_d as a fitting parameter.

The donor ionization energy in Fig. 9 begins to increase at pressures lower than the $E_{d\Gamma} - E_{dX}$ crossover pressure of 17 kbars. We attribute this behavior to the Sn donor level attached to the L minimum. The donor ionization energy measured from the lowest donor level to the lowest conduction-band minimum at a particular pressure is shown in Fig. 9 as a dashed line. The choice of $E_{dL} = 150 \text{ MeV}$ gives the best fit to the experimentally obtained ionization energies. We

have shown E_{dL} , together with $E_{d\Gamma} = 6 \text{ MeV}$ and $E_{dX} = 101 \text{ MeV}$, by the dashed line in Fig. 4. As can be seen in the figure, the donor level associated with the Γ minimum is the lowest donor level up to about 9 kbars. Then the donor level associated with the L minimum becomes the lowest in the pressure range 9 to 24 kbars, and at pressures higher than 24 kbars the donor level associated with the X minimum becomes the lowest.

V. COMPOSITIONAL DEPENDENCE OF THE HALL COEFFICIENT AND THE IONIZATION ENERGIES OF THE Sn DONOR IN $\text{Al}_x\text{Ga}_{1-x}\text{As}$: RESULTS AND DISCUSSION

Hall measurements at atmospheric pressure on $\text{Al}_x\text{Ga}_{1-x}\text{As}$ doped with Sn were made in the compositional range $x=0$ to $x=0.7$. Results for a

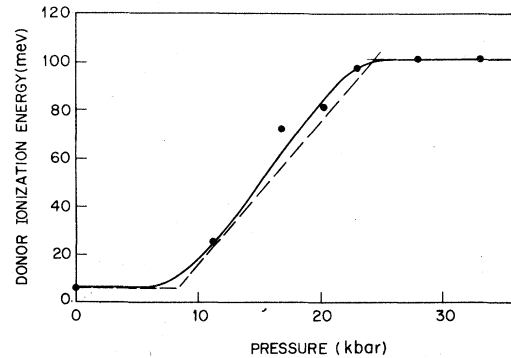


FIG. 9. The pressure dependence of the Sn donor ionization energy in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$. The solid line connects experimental data. The dashed line has been obtained from Fig. 4.

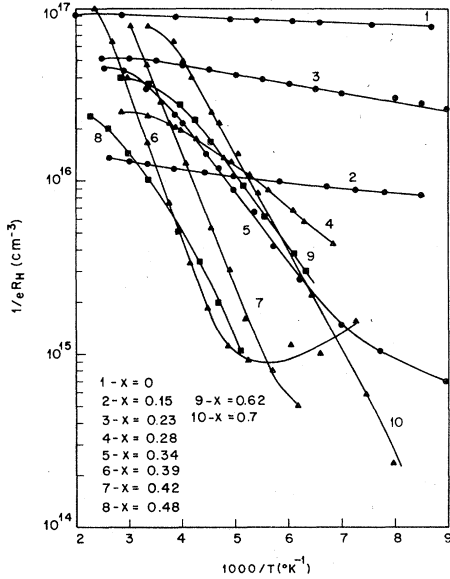


FIG. 10. The results of Hall measurements on some $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples.

few samples are shown in Fig. 10, where $1/R_H e$ is plotted as a function of $1/T$. We use the data to extract the ionization energies for the Sn donor and compare them with the results obtained in pressure experiments. The approach set out earlier has been adopted to analyze the data. The relative position of Γ , L , and X minima as a function of the compositional parameter x is shown in Fig. 11 by the solid lines. The direct-indirect Γ - X crossover occurs at $x=0.45$ at room temperature. The L minimum lies only slightly (~ 15 meV) above the band edge at the crossover.

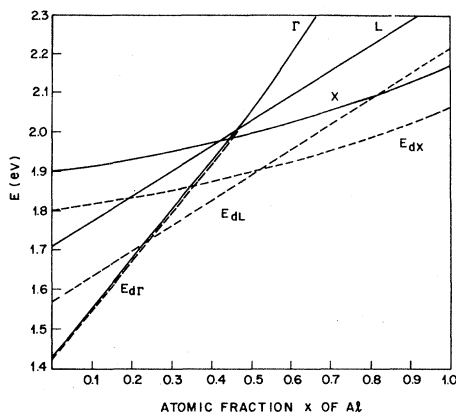


FIG. 11. The Γ , L , and X band energies plotted as a function of the compositional parameter x (Ref. 15). The donor levels attached to the minima are also shown by a dashed line.

TABLE II. Values of parameters of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ band structure and their compositional dependences (Ref. 15).

$$E_{g\Gamma}(x) = 1.424 + 1.247x \text{ eV}, \quad x < 0.45$$

$$1.424 + 1.247x + 1.147(x - 0.45)^2 \text{ eV}, \quad x > 0.45$$

$$E_{gL}(x) = 1.708 + 0.642x \text{ eV}$$

$$E_{gX}(x) = 1.900 + 0.125x + 0.143x^2 \text{ eV}$$

$$M_{\Gamma}(x) = (0.067 + 0.083x)M_0$$

$$M_L(x) = (0.55 + 0.12x)M_0$$

$$M_X(x) = (0.85 - 0.07x)M_0$$

In the region of composition close to crossover, conduction electrons populate all the three minima; hence the Hall coefficient R_H would be defined by expression (1). The α_i 's entering (1) have been calculated using the parameters of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ band structure given in Table II and are shown for $T=297$ and 167°K in Fig. 12. The L band now holds 40% of the electrons, compared to about 25% which it holds when the crossover is induced by pressure.

We will now use expression (1) to separate the freeze-out part from R_H^* in the experimental data of Fig. 10 and then we will find the donor ionization energy as a function of composition. In the present case, however, the procedure to obtain N_D and N_A is different from the approach used in the case of pressure experiments.

The temperature dependence of electron concentration permits assignment of donor and acceptor concentrations and the donor ionization energy. When Boltzmann statistics is applicable, these quantities are determined by the condition of electrical neutrality¹⁴:

$$\frac{n(N_A + n)}{\beta(N_D - N_A)N_c} = \exp\left(-\frac{E_d}{kT}\right). \quad (5)$$

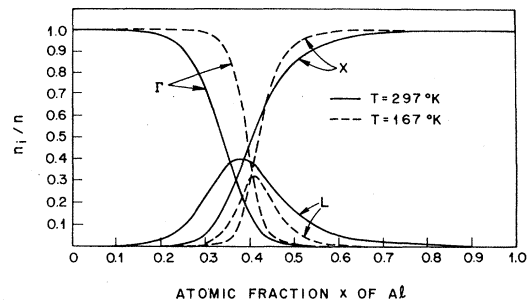


FIG. 12. Fractional electron concentration in the Γ , L , and X minima as a function of composition.

TABLE III. Parameters of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples used in the experiments.

Sample No.	x	$T = 297^\circ\text{K}$			$10^{16}N_D$ (cm^{-3})	$10^{16}N_A$ (cm^{-3})	E_d (meV)
		$\frac{1}{eR_H}$ (10^{16} cm^{-3})	n (10^{16} cm^{-3})	μ_H ($\frac{\text{cm}^2}{\text{V sec}}$)			
1	0.15	1.25	1.25	2980	8.4	7	6
2	0.23	5.0	5.5	2290	9	2	11
3	0.28	1.04	2.8	1870	12	5.2	40
4	0.34	3.47	5.72	1560	30	9.6	65
5	0.39	1.64	3.8	600	110	83.3	118
6	0.42	4.7	16.9	420	100	49	129
7	0.48	1.04	3.22	270	22	15.4	109
8	0.62	3.6	4.26	205	12	5.2	103
9	0.7	7.93	8.72	120	5	2.34	101

Plotting the logarithm of the left-hand side of expression (5) as a function of $1/T$, a linear dependence would result only for the right choice of $N_D - N_A$ and N_A . Then the slope of the line yields E_d . This procedure is extremely sensitive to $N_D - N_A$, though not so sensitive to N_A . Another fitting condition is that the resulting straight line should intercept the ordinate axis at the point where the logarithm of the left-hand side is equal to zero. This condition is sensitive to the choice of N_A . The result of the fitting and of some parameters of the samples used in the experiment are gathered in Table III.

The donor ionization energy is plotted as a function of the compositional parameter x in Fig. 13 (solid line). The curve has a well-defined maximum in the region of the crossover, reaching 130 meV and then decreasing to 101 meV. This can be explained if the donor levels attached to the conduction-band minima are assigned the following values of ionization energies: $E_{d\Gamma} = 5$ meV, $E_{dL} = 140$ meV, $E_{dX} = 101$ meV, as shown

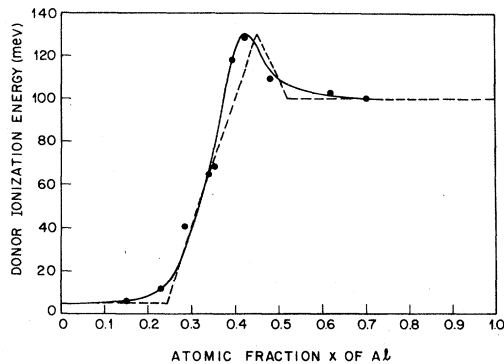


FIG. 13. The dependence of the Sn donor ionization energy as a function of x . The solid line connects experimental data. The dashed line was obtained from Fig. 11.

in Fig. 11 (dotted lines). With this system of donor levels, the compositional variation of the donor ionization energy measured from the lowest donor level to the lowest conduction-band minimum is shown in Fig. 13 as a dotted line. The agreement with experimentally obtained activation energies (solid line) is reasonable. Further, the value for E_{dL} , equal to 140 meV, agrees with the value for E_{dL} obtained from the high-pressure experiment. As can be seen in the figure, the donor level associated with the Γ minimum is the lowest in the range of x from 0–0.25, then the one associated with the L minimum becomes the lowest in the range of x from 0.25–0.52, and, eventually, the one associated with the X minimum becomes the lowest at $x > 0.52$.

Altarely and Iadonisi have shown¹⁶ that there is a strong interaction between the donor levels associated with the Γ and X bands. Our results do not appear to support the suggestion that this interaction is responsible for the presence of the maximum in the curve $E_d(x)$. If the latter were the case, a maximum should have occurred on the E_d curves for both pressure and composition (compare Fig. 9 with Fig. 13). The absence of a peak in the curve of donor ionization energy versus pressure and its presence on the curve of ionization energy versus composition can be explained by a slight difference in the position of the L minimum above the Γ - X crossover energy in these two cases (60 meV in the case of pressure versus 15 meV in the case of composition).

VI. SUMMARY AND CONCLUSIONS

A general approach to the problem of interpreting Hall data in the case of electronic conduction involving more than one conduction-band minimum is set out. This approach has enabled us to obtain the ionization energies of the Sn donor as a function of composition x in $\text{Al}_x\text{Ga}_{1-x}\text{As}$,

as well as in $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ as a function of pressure. The two results are consistent with the notion that the donor levels are associated with the Γ , L , and X conduction-band minima and are separated from the corresponding minima by 6, 140–150, and 101 meV, respectively. The difference in the shape of the donor ionization energy as a function of pressure, on the one hand, and composition, on the other, is explained by the difference in the position of the L band edge at the Γ - X crossover in these two cases. The elec-

tron mobility in the X minimum is found to be $120 \text{ cm}^2/\text{V sec}$ and shows no considerable variation with temperature.

ACKNOWLEDGMENTS

We wish to thank J. C. Hensel for many helpful discussions during the course of this study and R. G. Maines for much help in the pressure experiments.

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