# Shallow donorlike impurity states in $n$-type InP in magnetic field and under hydrostatic pressure

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Hall-coefficient and transverse magnetoresistivity measurements performed in magnetic fields up to 18 T and hydrostatic pressures up to 16.5 kbar reveal several features of the behavior of shallow donorlike impurity states in $n$-type InP with impurity concentrations spanning the metal-insulator transition ($2.2\times10^{15}$ cm$^{-3}\lesssim N_d-N_a\lesssim 6.2\times10^{16}$ cm$^{-3}$). At atmospheric pressure, the variation of the binding energy of the shallow donors versus magnetic field was found to follow the predicted hydrogenic behavior with increasing effects of electron correlations (screening of the long-range Coulomb potential) and overlap of impurity wave functions as the donor concentration increased. With increasing pressure, the binding energy increased only slightly up to $\sim$10 kbar, then much more strongly at 10 kbar $\lesssim P\lesssim$ 16.5 kbar. This behavior, which additionally depended on the actual magnetic field strength, showed very close similarities to effects observed earlier in other III-V compounds and suggests an increasing influence of the short-range localized impurity potential.

## I. INTRODUCTION

The combined effects of a magnetic field and hydrostatic pressure have proven to be an efficient tool for investigating the properties of apparently shallow donorlike impurity states both in magneto-optical[1-3] and transport experiments.[4-6] In low-effective-mass narrow-band-gap materials both perturbations can reach high intensities at readily accessible static magnetic fields and hydrostatic pressures, and unexpected effects have been observed in transport experiments[4-6] on samples with impurity concentrations ranging to values well above the Mott[7] critical density ($n_c$). In InP, where the energy gap is wider [$E_g\simeq1.423$ (Ref. 8)], and the electron-effective mass larger [$m_0^*\simeq0.815m_0$ (Ref. 9)], samples with impurity concentrations close to the metal-insulator transition must be used to observe similar effects.

Up to now, the effect of the magnetic field on shallow donors in InP has been reported in transport experiments.[10,11] However, in these works, the studies were restricted to a rather low-field range ($B<8$ T), and moreover, in one of them (Ref. 11), the investigation was limited to magnetoresistivity data only.

In this work, we have performed Hall-coefficient and transverse magnetoresistivity measurements on five samples of nominally undoped $n$-type InP ($2.2\times10^{15}$ cm$^{-3}\lesssim N_d-N_a\lesssim 6.2\times10^{16}$ cm$^{-3}$) in magnetic fields extending up to 18 T in the temperature range 3.6—27 K. One sample with $N_d-N_a=6.2\times10^{16}$ cm$^{-3}$ was additionally investigated under hydrostatic pressures of up to 16.5 kbar. At atmospheric pressure, and provided the magnetic field is high enough to induce a metal-insulator transition, the variation of the binding energy of the shallow donors versus magnetic field was found to follow the hydrogenic behavior predicted by the parabolic model of Larsen,[12] which has recently been shown[3,13,14] to yield an accurate picture of the effects in the magnetic field range investigated here ($\gamma=\hbar\omega_c/2R_y^*\simeq2$ at $B=18$ T in InP). At a given field, the binding energies were found to decrease with increases in the actual donor concentration of the samples. This behavior suggests the importance of the electron correlations which reduce the effective long-range Coulomb potential of the charged centers, even at low impurity concentrations, and the influence of the overlap of the impurity wave functions at higher concentrations. With increasing pressure, the binding energy of the shallow donors was found to increase first rather weakly up to $\sim$10 kbar than much more strongly at 10 kbar $\lesssim P\lesssim$ 16.5 kbar. The strong variation of the binding energy versus pressure at $P>10$ kbar, which was additionally enhanced by increasing the magnetic field strength, clearly indicates the influence of the strong and short-range (localized) impurity potential[15] as observed in other III-V materials: InSb,[1,3,5] GaAs,[2] and InAs,[6] from magnetotransport[5,6] and magneto-optical[1-3] experiments under pressure.

## II. EXPERIMENTAL PROCEDURE

$n$-type indium phosphide samples were cut from nonintentionally doped bulk crystals grown by liquid-encapsulated Czochralski pulling.[16] The samples with dimensions of about $5\times1.5\times0.3$ mm$^3$ were etched in a solution of 1% Br in methanol. In order to obtain low-resistance Ohmic contacts, six circular Au dots were deposited beforehand in a Van der Pauw configuration by thermal evaporation,[17] then six balls of high-purity (99.9999%) indium were alloyed by a heat treatment in flowing $H_2$ at temperatures $\sim$400 °C. The Ohmicity of the contacts was checked by current-voltage measurements.

Given in Table I are the characteristics of the samples used in this work as obtained from low-magnetic-field Hall coefficient ($R_H$) and zero-magnetic-field electrical resistivity ($\rho_0$) measurements at three different temperatures (room, liquid-nitrogen, and liquid-helium temperatures). The values of the Hall concentrations ($n_H=1/R_He$) and Hall mobilities ($\mu_H=R_H/\rho_0$) listed in Table I and their variations versus temperature are

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TABLE I. $n$-type InP sample characteristics at atmospheric pressure. $N_d-N_a$ is the net donor concentration, $n_H=1/R_He$ is the Hall concentration, and $\mu_H=R_H/\rho_0$ is the Hall mobility.

| Sample | $N_d-N_a$ ($cm^{-3}$) | $T=300$ K $n_H$ ($cm^{-3}$) | $\mu_H$ ($cm^2/V\,s$) | $T=77$ K $n_H$ ($cm^{-3}$) | $\mu_H$ ($cm^2/V\,s$) | $T=4.2$ K $n_H$ ($cm^{-3}$) | $\mu_H$ ($cm^2/V\,s$) |
|---|---|---|---|---|---|---|---|
| 1 | $6.2\times10^{16}$ | $5.2\times10^{16}$ | 2090 | $4.6\times10^{16}$ | 4310 | $3.6\times10^{16}$ | 372 |
| 2 | $2.2\times10^{16}$ | $1.8\times10^{16}$ | 4330 | $1.3\times10^{16}$ | 13 340 | $1.0\times10^{16}$ | 248 |
| 3 | $1.02\times10^{16}$ | $8.5\times10^{15}$ | 4487 | $6.2\times10^{15}$ | 17 691 | $5.3\times10^{15}$ | 100 |
| 4 | $8.4\times10^{15}$ | $7.0\times10^{15}$ | 2972 | $5.0\times10^{15}$ | 18 360 | $7.5\times10^{14}$ | 33 |
| 5 | $2.2\times10^{15}$ | $1.8\times10^{15}$ | 3171 | $1.3\times10^{15}$ | 12 300 | $2.8\times10^{14}$ | 11 |

characteristic of samples close to the metal-insulator transition.[18,19] The net donor concentrations ($N_d-N_a$) obtained from $R_H$ measurements at 300 K by using a Hall factor $r=1.2$ (Ref. 20) span the Mott[7] critical density [$n_c=(0.25/a_H^*)^3\simeq3\times10^{16}$ $cm^{-3}$ in InP].

A homogeneous static high magnetic field (up to 20 T) was supplied by a 10-MW Bitter coil[21] at the Service National des Champs Intenses (SNCI) of the Centre National de la Recherche Scientifique (CNRS), Grenoble, France. High hydrostatic pressures up to 16.5 kbar were obtained in a Cu-Be clamp cell[22] containing a mixture of light hydrocarbons as the pressure transmitting medium.

The Hall coefficient and transverse magnetoresistivity were measured using a standard dc method in the 3.6–27 K temperature range. The measurements were always carried out for two current and two magnetic field directions, and at electric field values low enough to avoid sample heating and impact ionization of the donors.

## III. EXPERIMENTAL RESULTS

The effect of the magnetic field on the Hall coefficient ($R_H$) and transverse magnetoresistivity ($\rho_\perp$) revealed several quite similar features in the samples investigated. These effects will therefore be illustrated below by the results from samples 1 and 5 at the two extremes of the impurity concentration range investigated here. As shown in Figs. 1 and 2, the $R_H$ and $\rho_\perp$ versus magnetic field behaviors clearly depended on the temperature range considered.

At $T<10$ K, $R_H$ showed an anomalous behavior versus magnetic field in sample 1 as seen at different temperatures in the inset of Fig. 1(a), and the Hall effect became scarcely detectable as the impurity concentration decreased toward sample 5. This effect, which coincided with the appearance of a negative magnetoresistance at low fields ($B<3$ T), suggests an increasing influence of localization effects as observed by Biskubski *et al.*[23] and Long and Pepper,[24] and will be considered elsewhere.

At $T\gtrsim10$ K, the temperature-dependent strong increase in both $R_H$ and $\rho_\perp$ versus magnetic field are in turn characteristic of magnetic-field-induced deionization of donorlike impurity states as usually observed in magnetic freeze-out experiments.[4–6,10] Therefore, only this temperature range is further considered in this work.

The comparison between the freeze-out effects in sample 1 and those observed in sample 5 shows quite distinct features. In contrast with the rather weak temperature dependence of the low magnetic field ($B<5$ T) $R_H$ in

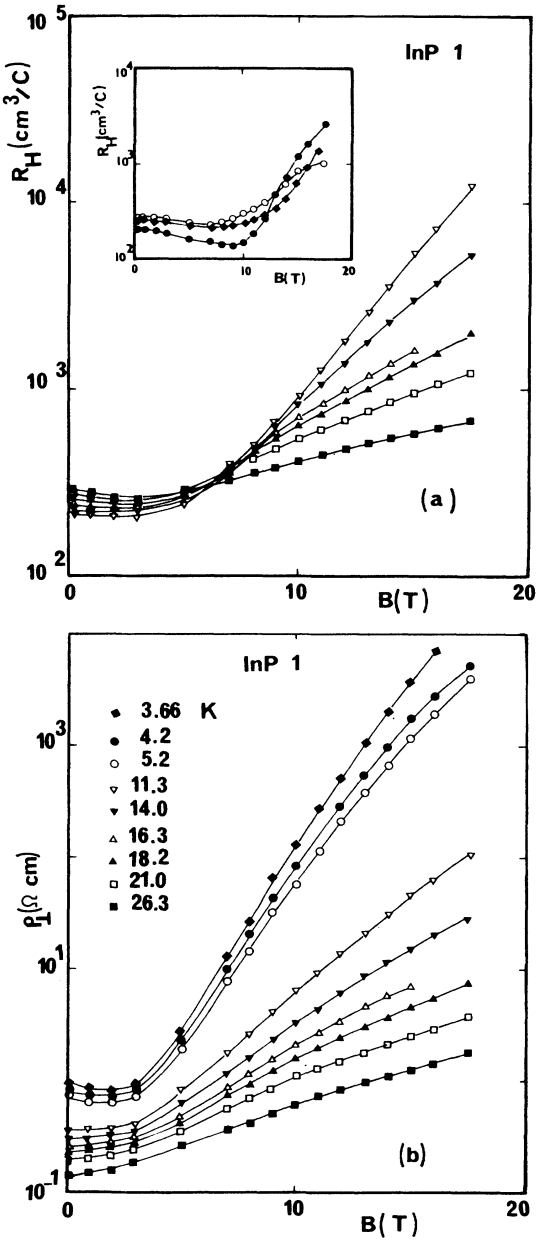


FIG. 1. (a) Hall coefficient and (b) transverse magnetoresistivity vs magnetic field for sample 1 at atmospheric pressure and various temperatures. Typical anomalous behavior of the Hall coefficient vs magnetic field at $T<10$ K is shown in the inset of (a).

sample 1 [Fig. 1(a)], the low field $R_H$ in sample 5 decreased by almost one order of magnitude with increasing temperature from 10.1 to 25 K [Fig. 2(a)]. The latter behavior indicates that in sample 5, the impurity level is already separated from the bottom of the conduction band even in the absence of the magnetic field.

The effect of hydrostatic pressure on the variations of $R_H$ and $\rho_\perp$ versus magnetic field is shown in Fig. 3 for sample 1 at $T=14$ K. As can clearly be seen, there are two ranges of pressure. At $P$ up to $\sim 10$ kbar, the $R_H(B)$ and $\rho_\perp(B)$ variations were only slightly affected, while at higher pressures, an appreciable increase in $R_H$ and $\rho_\perp$ occurred starting at low magnetic fields, and this effect was enhanced as the magnetic field increased. With decreasing temperature, these combined effects of hydrostatic pressure and magnetic field became stronger.

## IV. ANALYSIS

In order to analyze the data, we assume the existence of an impurity level and we start with the neutrality equation, written as follows:

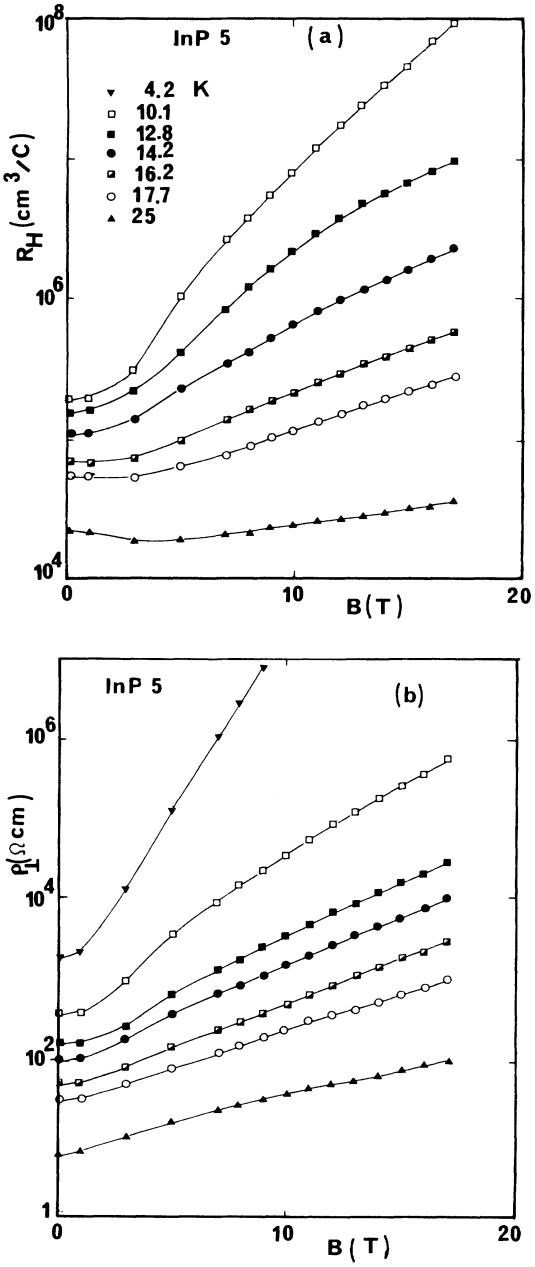


FIG. 2. (a) Hall coefficient and (b) transverse magnetoresistivity vs magnetic field for sample 5 at atmospheric pressure and different temperatures.

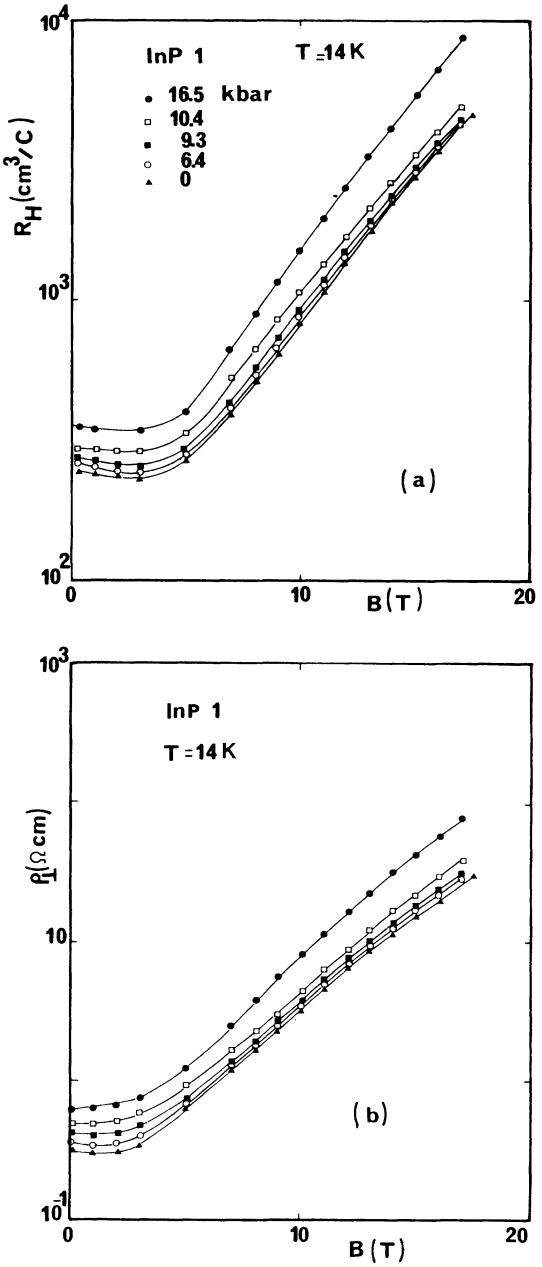


FIG. 3. (a) Hall coefficient and (b) transverse magnetoresistivity vs magnetic field for sample 1 at $T=14$ K and for several values of the pressure.

$$N_d - N_a = n + \frac{N_d}{1+(1/g)\exp[(E_I - E_F)/k_B T]} , \quad (1)$$

where $N_d$ and $N_a$ are the concentrations of donors and acceptors, respectively, $n$ is the free-carrier concentration, $g$ is the degeneracy factor, $E_I$ is the activation energy of the donor level, and $E_F$ is the Fermi energy.

As discussed in a previous paper,[6] in the absence of exact information about donor and acceptor concentrations, we are forced to analyze the data in steps using simplifying assumptions. It should be pointed out that this complication cannot be avoided by analyzing the low-temperature mobility data, since it is now well established[25] that at impurity concentrations close to the metal-insulator transition, the Brook-Herring theory breaks down, and the analysis is no longer straightforward.

As a first step, we must determine the free-carrier concentrations and their distribution among Landau levels. This is done in Sec. IV A below. In Secs. IV B and IV C, we use two methods to determine the ionization energies and the approximate values of donor and acceptor concentrations.

### A. Variations of the free-carrier concentrations

The general formula of $R_H$ is written as follows:

$$R_H = \frac{1}{B}\frac{\sigma_{xy}}{\sigma_{xx}^2+\sigma_{xy}^2} , \quad (2)$$

where $B$ is the magnetic field induction along the $z$ axis and $\sigma_{xx}$ and $\sigma_{xy}$ are the diagonal and off-diagonal conductivity tensors, respectively.

In the case of high-mobility narrow-band-gap materials (such as InSb and InAs), $\omega_c\tau$ becomes much higher than 1 at high fields, and it is an experimental fact that $\sigma_{xx}$ is always greater than $\sigma_{xy}$ in the magnetic freeze-out regime.[26,4,6] Therefore, the free-carrier concentrations must be determined from the high-field formula.[26,4,6]

In the case of InP, considered here, $\omega_c\tau$ remained not far above 1 up to the highest fields, and $\sigma_{xx}$ was found to be smaller than $\sigma_{xy}$ in the temperature range of interest ($T > 10$ K). Therefore, we must use the simple formula for the free-carrier concentration, namely,

$$n = 1/R_H e . \quad (3)$$

Equation (3) is expected to give $n$ with good accuracy at fields high enough so that $\omega_c\tau > 1$ and the Hall factor $r \to 1$. This holds for the samples studied at $B \gtrsim 5$ T.

Next, since we are concerned with a relatively high temperature range ($10\ \text{K} \lesssim T \lesssim 25$ K) and in view of the rather small cyclotron energy shift of the Landau levels expected in InP [high $m_0^*$ and small effective Landé factor $g_0^* \cong +1.2$ (Ref. 27)], we must determine the effective contribution of each Landau level to the observed effects. This was obtained by fitting the free-carrier concentration data derived from Eq. (3), using an appropriate model for the quantized nonparabolic conduction band[28] as given in detail in our previous work [Eqs. (6)–(12) of Ref. 6]. The parameter values used in the calculations both with and without pressure are given in Table II.

TABLE II. Parameter values of InP used in the calculations.

| Parameter | Value | Reference |
|---|---|---|
| $E_g(0)$ | 1.423 (eV) | 8 |
| $\Delta$ | 0.108 (eV) | 8 |
| $m_0^*(0)$ | 0.0815 ($m_0$) | 9 |
| $T\frac{\partial E_g}{\partial T}$ | $-4.91\times10^{-4}\frac{T^2}{(327+T)}$ (eV) | 20 |
| $\frac{\partial E_g}{\partial P}$ | $+9.5\times10^{-3}$ (eV/kbar) | 29 |
| $g_0^*(0)$ | +1.23 | 27 |

Figures 4(a) and 4(b) show the variations versus magnetic field of the total free-carrier concentrations ($n$) and their distribution among the lowest four Landau sublevels ($0^-$, $0^+$, $1^-$, and $1^+$) as obtained in sample 1 at $T = 11.3$ K and sample 5 at $T = 10.1$ K. As clearly seen in these figures, whereas the occupation of the $1^-$ and $1^+$ Landau sublevels (and therefore all higher sublevels) can obviously be neglected in the field range considered ($B \gtrsim 5$ T), both $0^-$ and $0^+$ must be taken into account. Similar calculations at higher temperatures showed that this is true for the whole temperature range. This clearly means that the conduction band must be considered to be quantized at $B \gtrsim 5$ T but the spin degeneracy is hardly lifted. In other words, the spin-degeneracy factor $g$ must be taken as equal to 2 in Eq. (1).

At lower fields ($B < 5$ T), the results must be analyzed within the framework of classical transport by taking into account that there is a range of fields $3\ \text{T} < B < 5$ T where the Landau level formation must set in, and neither of the two descriptions may be accurate.

### B. Determination of the activation energies from the slopes of $\ln(nT^{-1/2})$ versus $1/T$ curves at $B \gtrsim 5$ T

In a first approximation, the ionization energies of the donors can be obtained directly from the slopes of $\ln(nT^{-1/2})$ versus $1/T$ [see Eqs. (3) and (4) of Ref. 6], thus avoiding the complications arising from $N_d$ and $N_a$ values.[4,6] However, this method is expected to be accurate only if the nonparabolicity effects can be neglected and if the magnetic field is high enough to satisfy $n \ll N_a$ and $n \ll N_d - N_a$.

In the magnetic freeze-out experiments reported here, we are dealing only with the two lowest Landau sublevels as was shown in Sec. IV A above. Therefore, since the cyclotron energy shift of these two Landau sublevels ($0^+$ and $0^-$) always remains much smaller than the imperturbed energy gap in InP, the nonparabolicity effects should have a negligible contribution as observed in far-infrared magneto-absorption experiments.[9(b)] Furthermore, the condition $n \ll N_d - N_a$ could be readily verified from results such as in Figs. 4(a) and 4(b), and there was always a range of temperatures wide enough for this condition to be satisfied. Accordingly, the ionization energies obtained from the slopes of the plots such as those in

Figs. 5(a) and 5(b) can be considered to be quite accurate on condition that the samples be relatively compensated to satisfy $n \ll N_a$. This last condition will be checked in the following section.

The ionization energies obtained from the slopes of $\ln(nT^{-1/2})$ versus $1/T$ are shown in Fig. 6(a) for all the samples at atmospheric pressure, and in Fig. 6(b) for sample 1 at different pressures.

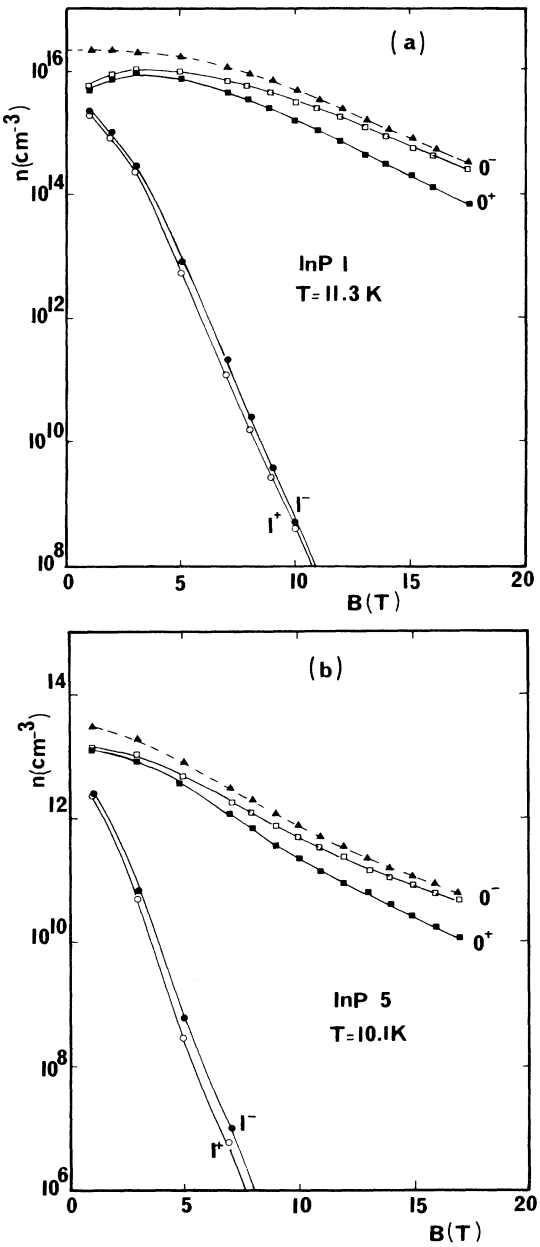


FIG. 4. Variation vs magnetic field of the total free-carrier concentration ($n$) and its redistribution between the four lowest Landau levels ($0^-$, $0^+$, $1^-$, and $1^+$) for samples 1 at $T=11.3$ K and 5 at $T=10.1$ K, respectively. The populations of the different Landau levels were calculated (see the text) by fitting the experimental values of $n$.

### C. Determination of the ionization energies from the graphic solution of the neutrality equation

This second method was used by Raymond *et al.*[30] in the case of InSb, and is based on the following:

Equation (1) can be written such that the only unknowns are $E_I$ and the compensation ratio $K=N_a/N_d$. Furthermore, $K$ is a characteristic of the sample which depends neither on the magnetic field nor on the temperature. Now, if we assume that the ionization energy is temperature independent, then there is only one value of

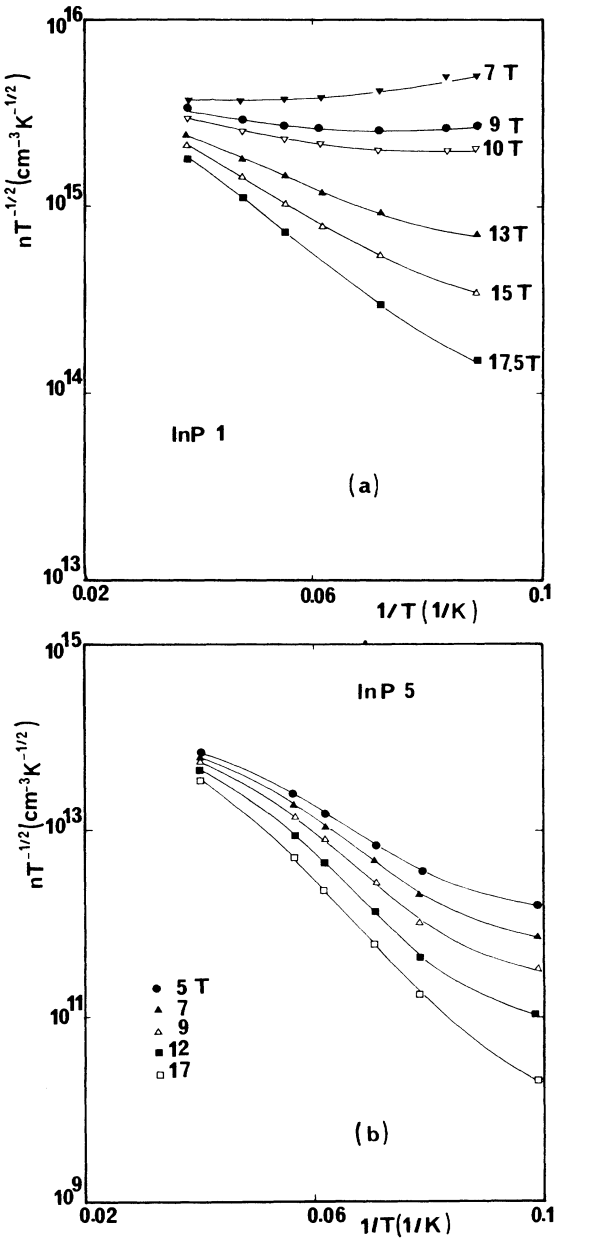


FIG. 5. Variation of $nT^{-1/2}$ as a function of $1/T$ at different magnetic fields. In sample 1, activated behavior appears only at $B>7$ T, while in 5 this is readily observed starting at the lowest fields.

$E_I$ at all temperatures and at a given magnetic field. In other words, if we plot $E_I$ versus $K$ at a fixed $B$ through Eq. (1), there will be a common intercept of the curves at different temperatures, thus giving the value of the ionization energy at the magnetic field considered, and the value of $K$ of the given sample.

Two such plots are shown in Figs. 7(a) and 7(b). It can be seen that when the field was high enough, we were always able to find a temperature range where the $E_I(K)$ curves had a common intercept. However, the procedure was not in general ideal, in that the intercepts at various fields did not yield a single value of $K$. Because the distribution of $K$ values was not wide and did not strongly affect $E_I$ values, it was possible to use the averaging procedure described by Raymond *et al.*[30]

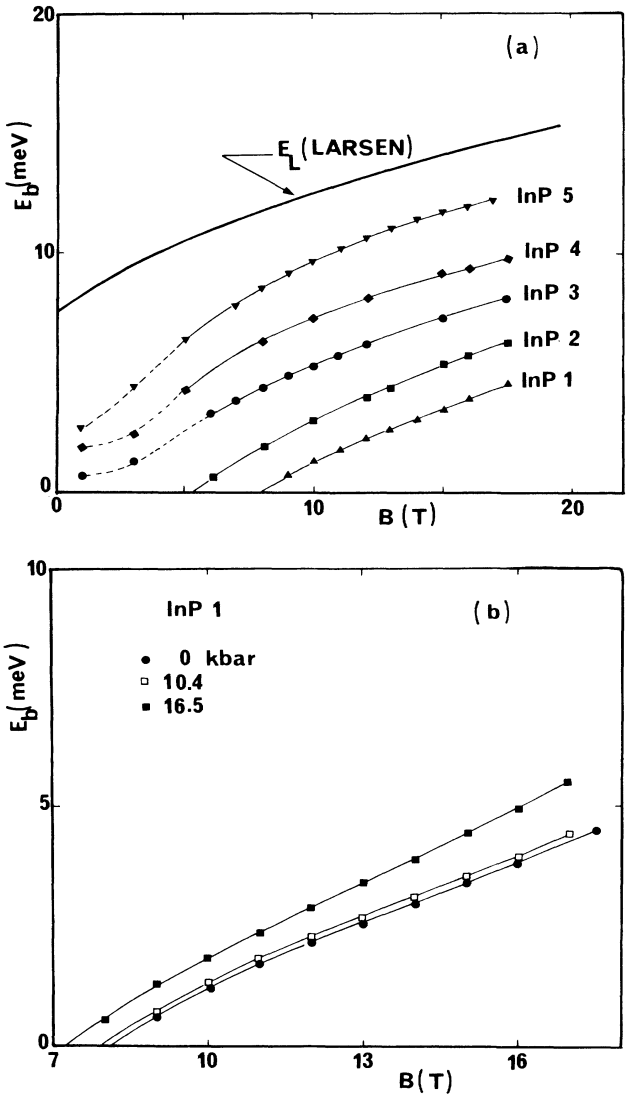


FIG. 6. Binding energies of the shallow donors as a function of the magnetic field in InP. Points are experimental values deduced as explained in the text. The solid line ($E_L$) is the theoretical prediction of Larsen (Ref. 12). The solid lines through the experimental points at $B \gtrsim 5$ T are calculated by solving the neutrality equation and by using $K = N_a/N_d$ obtained by method II. The dashed lines at $B < 5$ T are obtained by interpolation between low and high field data.

In Table III, the energies obtained by this method, hereafter referred to as method II, are compared for a few examples with those obtained from the slope method described in Sec. IV B above (method I). In general, there was good agreement between the two methods in the high-magnetic-field range ($B > 9$ T) with a difference not exceeding a few percent, within the accuracy of both the slope method ($\Delta E \cong 0.1$ meV) and method II ($\Delta E \cong 0.2$ meV). At lower fields ($5\ \text{T} \lesssim B \lesssim 9$ T), method II tended to give somewhat higher energies than method I, and this effect was greater in samples with smaller net donor concentrations, as observed by Raymond *et al.*[30] in InSb. Although the reasons for this effect were not clear,[30] both methods should lead, at least in our case, to somewhat larger errors with decreasing magnetic fields. This will be true for method I because the conditions $n \ll N_a$ and $n \ll N_d - N_a$ are less fully satisfied. Method II in turn may crucially depend on the broadening of the energy levels (thermal, overlap, disorder effects, etc.) which may become significant as the magnetic field decreases in this range where $\gamma = \hbar\omega_c/2R_y^* < 1$ and $\omega_c\tau$ decreases towards 1. This eventuality is strongly supported by the fact that with decreasing $B$, the $E_I(K)$ curves at different temperatures not only tended not to cross at the same point, but yielded a broadened pattern [see Fig. 7(a)]. This is also the more probable reason for which we were not able to use method II in the case of InAs.[6]

The compensation ratio values obtained from method II are given in Table IV. In it interesting to note that the actual $K$ values were found to be clearly correlated with the mobility data in the temperature range considered ($T > 10$ K), but much lower than those obtained from the Brooks-Herring ionized impurity scattering analysis. The values of $K$ given in Table IV show that the samples studied were rather compensated, and therefore the condition $n \ll N_A$ (see Sec. IV B) was largely satisfied in the magnetic field range considered ($B \gtrsim 5$ T). This means that method I gives quite an accurate description of the ionization energies as confirmed by solving the neutrality equation [Eq. (1)], and by using the $K$ values obtained from method II [solid lines in Figs. 6(a) and 6(b) at $B \gtrsim 5$ T].

## V. DISCUSSION

### A. Binding energy of the shallow donors at atmospheric pressure and various impurity concentrations

The ionization energies obtained in this way, and given in Fig. 6(a) for the five samples with different $N_d - N_a$ concentrations, clearly indicate that the effect of the magnetic field is to induce a metal-insulator transition (7). This happens as a result of the appearance and/or the increase in a finite binding energy ($E_b$) of shallow donorlike impurity states at fields high enough to shrink the impurity wave functions.[31]

In samples 1 and 2, where the impurity concentrations were higher than the Mott critical density ($N_d > n_c$ as

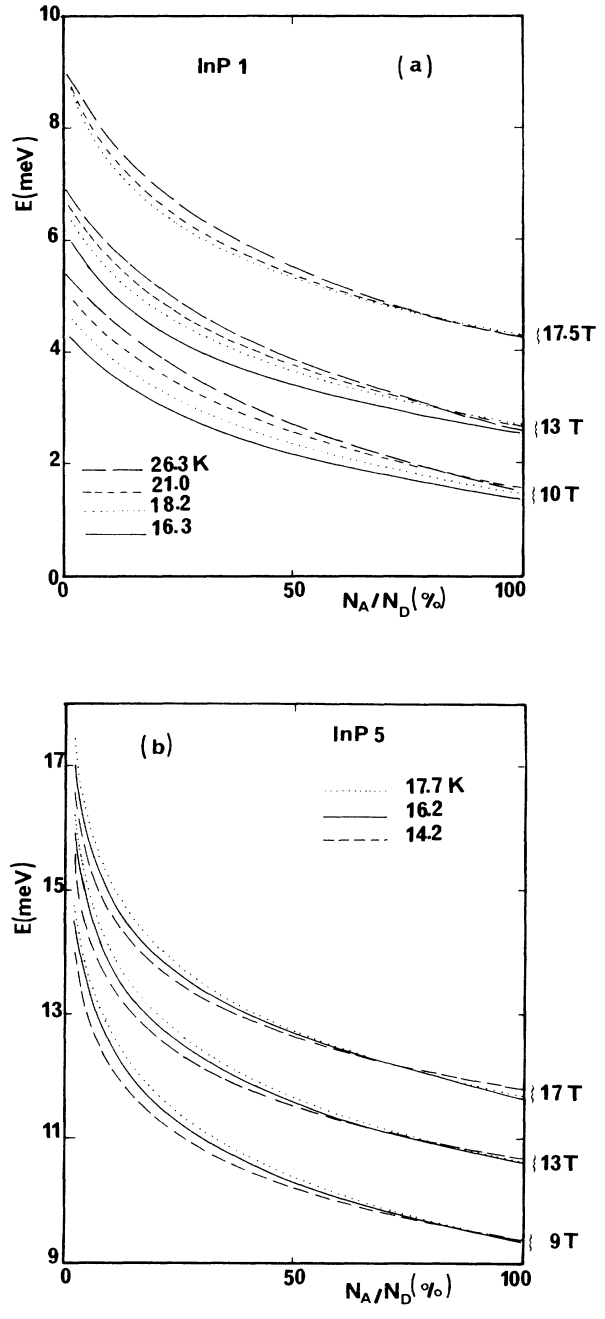


FIG. 7. Variation of the donor ionization energy vs compensation ratio for samples 1 and 5 at different temperatures and magnetic fields.

seen in Table IV), the binding energy could only be observed above a threshold field ($B_c$) which appears to be correlated with the actual donor concentration through the Mott criterion in the presence of a magnetic field.[32]

In samples 3, 4, and 5, where $N_d$ was below $n_c$, a finite binding energy was observed starting at low-field values. At $B \lesssim 3$ T, the energies were obtained for these samples using the low-field procedure [i.e., the slopes of $\ln(nT^{-3/2}$ versus $1/T)$], and the error bars are related to the uncertainties in the Hall factor ($r$) values since $\omega_c\tau \lesssim 1$ in this field range.

As pointed out in Sec. IV A, the impurity levels are difficult to determine in the magnetic field range $3 \lesssim B \lesssim 5$ T where the Landau-level formation sets in, and therefore, we only made interpolation between low- and high-magnetic-field data, as indicated by the dashed lines in Fig. 6(a).

At high fields ($B \gtrsim 5$ T), the variation of the energies versus magnetic field are observed to follow the theoretical prediction of the variational parabolic calculation of Larsen.[12] This model is known to give an accurate description of the variation of the ionization energy of an hydrogenic impurity in the low-$\gamma$ range of interest to us, as it has recently been shown both from a multiband adiabatic approach,[3,13] and from an expansion-variational procedure.[14] However, the absolute values of the experimental energies are much below the theoretical values. To account for this difference in magnetic freeze-out experiments, several mechanisms are usually considered:

(i) Correlation between conduction electrons (screening by free electrons).[33]

(ii) Correlations between bound electrons; screening by fixed charges,[34] and local dielectric constant enhancement via the polarization of neutral impurities.[35]

(iii) Broadening of the energy levels as a result of the overlap of the impurity wave functions.[36]

(iv) Broadening of the energy levels as a result of disorder effects.[37,38]

At impurity concentrations close to the metal-insulator transition, it is generally very difficult to discriminate between the respective contributions of these effects. However, as can be seen in Fig. 6(a), the decrease in $E_b$ is clearly correlated with the net donor concentrations $N_d - N_a$, not with the compensation ratio ($K$). This suggests that in the temperature range of interest ($T > 10$ K), the reduction of the binding energy of the donors below the hydrogenic value ($E_L$) must first of all be attributed to correlation effects and to the overlap of the impurity wave functions.

At low-impurity concentrations ($N_d < n_c$) and high

TABLE III. Comparison between the ionization energies $E_I$(I) and $E_I$(II) obtained by the two methods described in Secs. IV B and IV C, respectively.

| | Sample 1 | | Sample 5 | |
|---|---|---|---|---|
| $B$ (T) | $E_I$(I) (meV) | $E_I$(II) (meV) | $E_I$(I) (meV) | $E_I$(II) (meV) |
| 7 | | | 7.7 | 8.6 |
| 10 | 1.3 | 1.5 | 9.6 | 10.1 |
| 13 | 2.5 | 2.6 | 10.9 | 11.2 |
| 17 | 4.3 | 4.4 | 12.1 | 12.3 |

TABLE IV. Values of the compensation ratio ($K=N_a/N_d$) and the donor concentrations obtained by the method described in Sec. IV C. The Hall mobilities at $T=14$ K shown in the last column are clearly correlated with $K$.

| Sample | $K=N_a/N_d$ (%) | $N_d$ ($cm^{-3}$) | $\mu=R_H/\rho$ at $T=14$ K ($cm^2/V\,s$) |
|---|---|---|---|
| 1 | 78±5 | $(3.0\pm0.7)\times10^{17}$ | 1190 |
| 2 | 50±5 | $(4.4\pm0.4)\times10^{16}$ | 2230 |
| 3 | 52±5 | $(2.2\pm0.2)\times10^{16}$ | 2898 |
| 4 | 30±5 | $(1.2\pm0.1)\times10^{16}$ | 7670 |
| 5 | 75±5 | $(9.2\pm0.2)\times10^{15}$ | 1098 |

magnetic fields, owing to the strong freeze-out effect, the screening by free electrons must become negligible, and correlatively, the concentration of neutral donors must increase. Therefore, the variation of $E_b$ versus $N_d-N_a$ as shown in Fig. 8 can be related to dielectric-constant enhancement due to polarization of neutral donors as $N_d\rightarrow n_c$ from the insulating side.[39,40] At $N_d>n_c$, an increasing influence of the overlap of the impurity wave functions and screening by free electrons is expected to reduce $E_b$ further.[40]

It is interesting to note that, as was observed previously in InSb,[4] the overall variation of $E_b$ versus $N_d-N_a$ at high fields can be well described by the mechanism first put forward by Pearson and Bardeen,[41] i.e., $E_b=E_L-\alpha(N_d-N_a)^{1/3}$, on condition that $\alpha$ [$\alpha\cong2.65e^2/\chi$ (Ref. 41)] is taken to be smaller than the theoretical prediction (see Fig. 8).

### B. Combined effects of magnetic field and hydrostatic pressure on the binding energies of the donors

As shown in Fig. 6(b), the binding energy of the donors increases with increasing pressures. However, as can clearly be seen in Fig. 9, this effect is found to depend both on the pressure and on the magnetic field range considered. The binding energy of the shallow donors first increased only slightly at low pressures up to about $\sim10$ kbar, then a stronger increase set in at higher pressures. Moreover, the strong increase at high pressures clearly depended on the magnetic field strength in that it was further enhanced as $B$ increased.

The increase in $E_b$ at low pressures ($P<10$ kbar) can be approximated by a linear rate of $10^{-2}$ meV/kbar which, within the accuracy of the results, can be well accounted for by an effective-mass framework. However, the features revealed by the combined effects of pressures higher than 10 kbar and high magnetic fields are no longer consistent with hydrogenic behavior. In the pressure range 10.4—16.5 kbar, the pressure coefficient at $B=12$ T was in fact found to increase by one order of magnitude with respect to its low-pressure value (Fig. 9), and was moreover enhanced about twofold when the magnetic field increased to 17 T. These effects are clearly related to an increasing localization of the impurity wave functions under the influence of both hydrostatic pressure and magnetic field, and consequently, suggest a growing contribution by the short-range component (V s) of the impurity potential.[15] Also consistent with an increasing localization[15] is the fact that at $P=16.5$ kbar, the variation of $E_I$ versus $B$, as shown in Fig. 6(b), tended to a linear rate $dE_I(B)/dB\simeq0.55$ meV/T very close to the shift ($\frac{1}{2}\hbar\omega_c-\frac{1}{2}\mu_B g_0^* B$) of the lowest Landau level itself with respect to the top of the valence band.

Our observations in InP of the behaviors of the apparently shallow donorlike impurity states versus magnetic field and pressure are very similar to previous observations in a variety of III-V compounds: InSb,[1,3,5] InAs,[6] and GaAs,[2] in magnetic freeze out[5,6] and in magneto-optical[1-3] studies under pressure. In all these materials, the common feature is an abrupt pressure-induced deepening of donorlike impurity states which initially (at $P=0$ kbar) behave as shallow states. This effect always coincides with the existence of non-Γ-like energy levels, form-

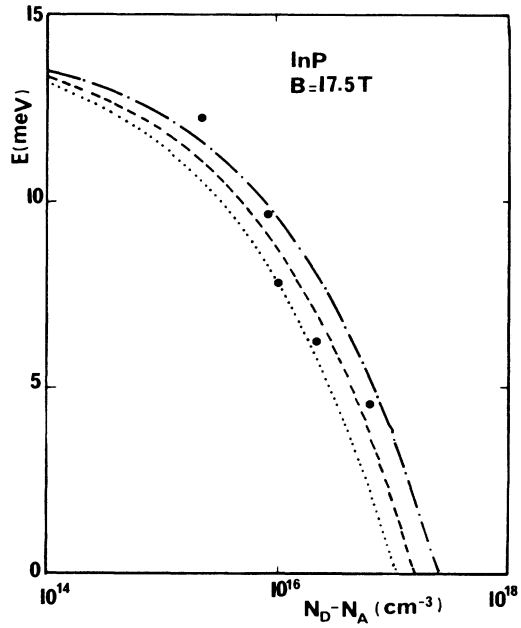


FIG. 8. Variation of the donor binding energy at $B=17.5$ T as a function of the net donor concentration ($N_d-N_a$). The different curves plotted through the data points are obtained by assuming a variation of the form predicted by Pearson *et al.* (Ref. 41) [$E_b=E_L-\alpha(N_d-N_a)^{1/3}$] with different values of $\alpha$. The dotted curve corresponds to the rough estimate $\alpha=2.65e^2/X$ (Ref. 41) which gives $\sim3.15\times10^{-5}$ meV cm in InP. The dashed and the dashed-dotted curves were obtained by assuming $\alpha=2.75\times10^{-5}$ meV cm and $\alpha=2.35\times10^{-5}$ meV cm, respectively.

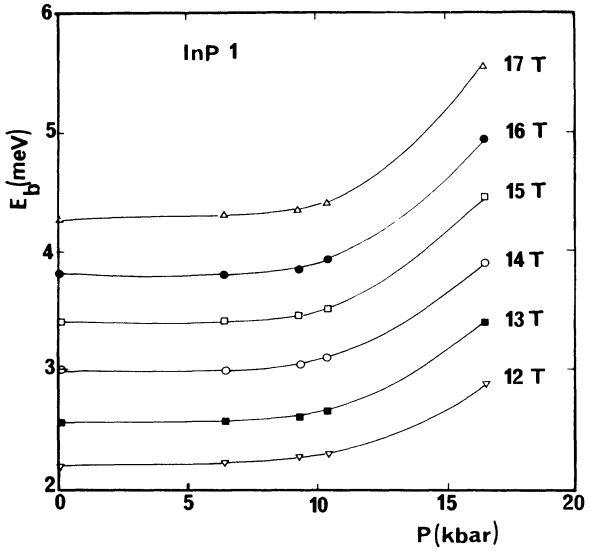


FIG. 9. Variation of the donor binding energy vs pressure at different values of the magnetic field for sample 1.

ing localized resonances in the conduction-band continuum, which are driven into the fundamental gap under pressure. Moreover, at least in the case of InSb, the resonant states are known to be strongly coupled to the lattice.[42]

To our knowledge, no similar studies conducted under pressure have yet been reported in the case of InP. However, at atmospheric pressure, both photoluminescence (PL) studies[43] and far-infrared photoconductivity (FIRPC) measurements[44,45] have shown a well-resolved central-cell structure correlated with residual group-VI and group-IV contaminants, with a main contribution from sulfur and silicon depending on the growth technique.[43] In bulk-grown liquid-encapsulated Czochralski crystals such as those used in this work, the FIRPC spectra[44,45] suggest the presence of a large number of residual donors (about 12), but with four well-resolved components.[45] These features are also characteristic of other III-V compounds, such as GaAs and InSb, which have been thoroughly investigated. In both cases, it has been shown[1-3] that the deepest of the four components, usually labeled $A$ in InSb, exhibits an anomalous behavior (deep-level-like) when pressure is applied.

In our transport data, we are of course unable to discriminate between the various central-cell contributions. However, the close similarities between the results we obtained here for InP and previous magneto-transport data in other III-V compounds[5,6] suggest that the effects may be detectable in magneto-optical experiments under pressure.

## VI. SUMMARY AND CONCLUSIONS

Magnetic freeze-out experiments have been performed at B up to 18 T on a series of unintentionally doped bulk-grown InP crystals with carrier concentration spanning the Mott critical density ($2.2\times10^{15}$ cm$^{-3}\lesssim N_d-N_a\lesssim 6.2\times10^{16}$ cm$^{-3}$). The experiments were also performed versus pressure (up to 16.5 kbar) in the most doped sample ($N_d-N_a\cong 6.2\times10^{16}$ cm$^{-3}$). The data showed the following features for the shallow donorlike impurity states.

At atmospheric pressure, the variation of the binding energy of the donors versus magnetic field was found to follow the predicted hydrogenic behavior but with a strong reduction in absolute values as the actual donor concentration of the samples increased. In agreement with a magnetic-field-induced metal-insulator transition, this behavior suggested the influence of electron correlations and overlapping of the impurity wave functions as the donor concentration changed.

With increasing pressure, the binding energy of the donors was found to increase, first only slightly up to $\sim 10$ kbar, then much more strongly at 10 kbar $\lesssim P\lesssim 16.5$ kbar. These effects, which were enhanced as the magnetic field increased, gave clear evidence for an increasing localization of the apparently shallow impurity states in almost the same way as observed in other III-V materials both from magnetotransport and magneto-optical studies under pressure.

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