PHYSICAL REVIEW B VOLUME 40, NUMBER 6 15 AUGUST 1989-II

High pressure and DX centers in heavily doped bulk GaAs

T. Suski, R. Piotrzkowski, P. Wiśniewski, E. Litwin-Staszewska, and L. Dmowski
High Pressure Research Center (UNIPRESS), Polish Academy of Sciences, ulica Sokołowska 29, PL-01-142 Warszawa, Poland
(Received 23 March 1989)

Measurements of the pressure dependence of electron concentration and mobility have been analyzed for heavily doped, bulk GaAs:(Si,Sn,S,Te). It is demonstrated that the samples with $n > 2\times10^{18}$ cm^{-3} exhibit the effect of carrier freeze-out for pressures below 20 kbar. GaAs:Te represents the exception to this behavior (n versus pressure is constant up to 25 kbar). Two models of the localized state of the donor are considered. Neutral, DX^0, or negatively charged, DX^-, states might appear after trapping one or two electrons, respectively, by the positively charged donor center. The results obtained show that the energetic level related to the DX center, E_{DX}, is located much higher in the conduction band than could be deduced from results extrapolated from $Al_{1-x}Ga_xAs$ (E_{DX} situated about 170 meV above the bottom of the Γ conduction band, versus $E_{DX} > 250$ meV obtained in this work). The results show that the localized and metastable DX center is not related to any single conduction-band minimum; its energy position and pressure coefficient exhibit significant temperature dependence. For a Si donor in GaAs, weakening of the electron-lattice coupling strength as a result of applying pressure is anticipated. Increase of electron mobility with decreasing carrier concentration has been observed here. Though it is suggestive to use this result for eliminating the concept of the DX^- center, some objections to this conclusion, due to possible correlations in dopant distribution, are presented in the paper.

I. INTRODUCTION

Coupling of the electronic and crystal-lattice subsystems related to defects in semiconductors which leads to persistent photoconductivity[1] and metastable character of the carrier concentration[2] has very recently become the subject of considerable interest. Vacancies in Si,[3] CdTe:Cl[4] CdF_2,[5] and $Pb_{1-x}Sn_xTe$:In,[6] grain-boundary-induced effects in II-VI compound narrow-band-gap semiconductors[7] represent the considered class of phenomena. However, due to the technological importance, studies of the impurities with the lattice relaxation effect (LRE have been carried out extremely intensively in III-V compound semiconductors. For example, the following systems have been examined: InSb:O,[8,9] GaSb:S,[10] $Ga_{1-x}Al_xSb$:Te,[11] $EL2$ in GaAs,[12,13] and the DX center in $Al_xGa_{1-x}As$ and GaAs.[14–18] There are several problems and solving them seems to be of crucial importance for understanding the physics of DX centers. We will mention some of them.

(i) *Charge state of the DX center.* Until very recently the following picture was commonly adopted: a substitutional donor may bind an electron to form two different neutral states. The $\mathcal{d}^0$ state, introducing no lattice deformation in its vicinity, and a localized, neutral state exhibiting LRE, DX^0.[19] However, lack of an electron-paramagnetic resonance signal from the DX center has led to the proposal of a "negative U" defect center, i.e., a highly localized and negatively charged donor with LRE, DX^-.[20,21] This state appears after the capture of two electrons by the positively charged donor state, $\mathcal{d}^+$. The gain in energy accompanying the appropriate deformation of the donor vicinity (LRE) exceeds the energetic cost of binding the additional electron by the DX^- state.

(ii) *Character of the DX center.* The wave function of this state may consist of contributions from only one minimum of the conduction band, e.g., L minimum,[15] or a wide range of Brillouin-zone contributions have to be taken into account.[22]

(iii) *Energetic position of the localized state of DX in GaAs E_{DX}.* Extrapolation of E_{DX} from $Al_{1-x}Ga_xAs$ with $X > 0.22$ to GaAs suggests a resonant level lying about 170 meV above the Γ point of the conduction band for $x = 0$.[15] Application of hydrostatic pressure has enabled the very important finding of the DX center in GaAs.[23] As it has been reported very recently, this resonant donor level might become electrically active even at ambient pressure for the doping level as high as 1×10^{19} cm^{-3} and E_{DX} was located about 280 meV above the Γ band edge.[24]

(iv) *Microscopic origin of the DX center.* The situation evolved from a donor-defect complex[14] to a substitutional donor with large or weak LRE (Refs. 25 and 16) and very recently Chadi and Chang[21] have proposed a threefold-coordinated donor or one of its nearest neighbors on the interstitial site as a proper structural model of the DX center.

In this paper we will concentrate on the first three problems. For this purpose, measurements of the electric transport phenomena under high pressure for heavily doped n-type GaAs have been performed.

The experimental results consisting of the Hall coefficient changes enabled us to deduce the pressure dependence of electron concentration n. To obtain E_{DX} the transfer of electrons onto DX states was analyzed by means of the two models briefly described in (i). The aim

of the performed analysis was not to choose between these two approaches but more to demonstrate implications of the assumptions used. Particularly, the two resulting sets of data on the pressure shift of E_{DX} provide arguments against the relation between the localized state of the *DX* center and any of the conduction-band minima.

The important consequence of the LRE consists in a metastable redistribution of electrons between the conduction band and the deep state of the *DX* center. This effect becomes important below a certain temperature as the barriers for electron capture and emission on and from the *DX* state start to play a role.[26] Hydrostatic pressure may or may not influence the configuration-coordinate diagram[2] describing this situation. In the paper, the experimental examination of the relation between pressure and the conditions for appearance of a metastable occupation of the *DX* state is presented also.

The two models of the localized donor state, DX^0 and DX^-, imply different variations of the ionized center concentration in the process of the electron capture. In the former case, a change in the electron concentration causes the same change in the number of scattering centers. In contrast, the formation of DX^- does not change the scattering center density. One may expect that the analysis of the electron mobility dependence on carrier concentration will help in verifications of the two proposed concepts of the localized donor center. However, the observed increase or decrease of electron mobility with rising *n* in epitaxially grown heterostructures of $Al_xGa_{1-x}As$ (Ref. 27) pointed out some implications arising from the configuration of the complicated semiconductor systems (e.g., presence of a spacer).

Part of this paper is devoted to the examination of electron mobility in samples with various numbers of *DX* centers. The use of the bulk samples eliminates possible complications caused by band bending at surfaces, heterostructure interfaces, or doping profiles[28] which may result in appearance of macroscopic potential barriers[29] and their contribution to the phenomena generated by microscopic (*DX* center) barriers.

We have limited our studies to GaAs samples. As it has been recently reported[30] DLTS spectra of $Al_xGa_{1-x}As$ exhibited structure consisting of multicomponent peaks evolving with the substitution of Al for Ga atoms as the Al content is increased. This result was interpreted as originating from the statistical distribution of Ga and Al cations in the vicinity of the donor. Thus the various local alloy compositions seem to produce a multimodal structure of the *DX* center.

The Appendix is placed after a summary of the most important results of this work. It contains a consideration of the electron capture by DX^- states of the *DX* center. Thus, the respective relations between the carrier concentration and energy of the deep, localized donor state of DX^- are given there.

II. EXPERIMENT

The Hall coefficient R_H and resistivity as a function of hydrostatic pressure up to 26 kbar (at room temperature) and up to 20 kbar (at 77 and 4.2 K) were measured for heavily doped *n*-GaAs. Seven bulk samples [liquid-encapsulated Czochralski (LEC) and horizontal Bridgman] with Si, Sn, S, and Te as dopants were used. The electron concentration varied between 2×10^{18} and 7×10^{18} cm^{-3} (Table I).

For the majority of experiments, high-pressure clamp-cells with a liquid as a pressure-transmitting medium were used. For studies of the metastable occupancy of *DX* centers the He-gas compressor was applied. It allowed us to change pressure even at low temperatures (e.g., 77 K).

III. RESULTS AND DISCUSSION

A. Metastability

As was briefly mentioned in the Introduction, LRE leads to an important consequence. Namely, different

TABLE I. Sample characteristics: type of donor; free carrier concentration, *n*; temperature at which measurements were performed, *T*; energy of the *DX* state (estimated for ambient pressures), E_{DX^0}—determined for the neutral donor state; E_{DX^-}—for the negatively charged donor state; the respective pressure coefficients, dE_{DX^0}/dp and dE_{DX^-}/dp.

Donor	n (10^{18} cm^{-3})	T (K)	E_{DX^0} (eV)	E_{DX^-} (eV)	dE_{DX^0}/dp (eV kbar^{-1})	dE_{DX^-}/dp (eV kbar^{-1})
Si	4.2	300	415	588	14.0	18.4
	4.2	77;4.2	320	420	11.8	13.0
	3.25	300	393	547	14.1	18.9
	2.75	300	413	532	14.4	18.2
Sn	2.8	300	410		14.5	
	2.8	77	270		9.2	
S	5.5	300	437		18.0	
	3.3	300	390		17.0	
	3.3	77	324		14.1	
Te	7.0	300				

electronic states may be accompanied by different lattice deformations. One electron picture for impurity states is then inadequate and the total energy of the system "electron plus the lattice" is described on the configurational-coordinate diagram (CCD) (Fig. 1). Two parabolas correspond to two electronic states. For the situation considered in this paper one of the parabolas ($Q=0$) represents the band state. One may observe the thermally activated carrier capture onto the DX state across the energy barrier E_C. The opposite transitions lead to the thermally activated carrier emission to the conduction band (across E_E). The height of the barriers may be changed by the application of pressure.[2] The separation of the equilibrium coordinates for the considered electronic states causes the possibility of metastable (nonequilibrium) occupations of the two levels. Only above T_{max} does the equilibrium situation exist. In the lower-temperature region ($T_{min} < T < T_{max}$) time dependencies of various effects can be observed (Fig. 2). Then the pressure and temperature variation of the relaxation time τ, describing the decay of a metastable occupancy of impurity levels, can be used for determination of E_C and E_E. At $T < T_{min}$ the population of the impurity state with LRE remains metastable with a large magnitude of τ (e.g., days).

Below T_{min} the effects of persistent photoconductivity[1] (PPC) and a possibility of the persistent carrier concentration changes achieved by high-pressure freezeout (HPFO) of electrons onto DX centers have been observed.[31] The latter phenomenon may be generated by the procedure consisting of applying pressure at high temperatures ($T > T_{max}$) and releasing it at sufficiently low temperatures ($T < T_{min}$). Carrier concentration becomes insensitive to pressure changes at $T < T_{min}$, which enables one to obtain various occupations of the localized donor state at the same external conditions. Both processes (PPC and HPFO) could be useful to study those properties of a semiconductor which show a dependence

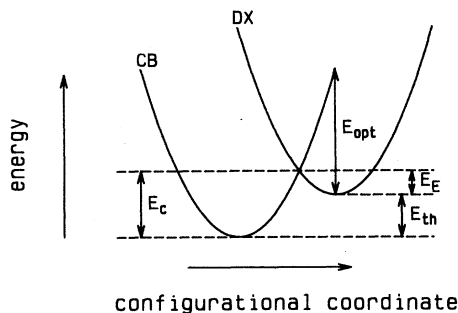


FIG. 1. A configuration-coordinate diagram showing the total energy of the impurity as a function of lattice distortion. The possible optical transition (from the localized donor state to the conduction band), E_{opt}, is marked. The barriers for capture and emission of electrons onto and from the localized state are denoted by E_C and E_E. Their difference is the thermal ionization energy $E_{th} = E_{DX}$.

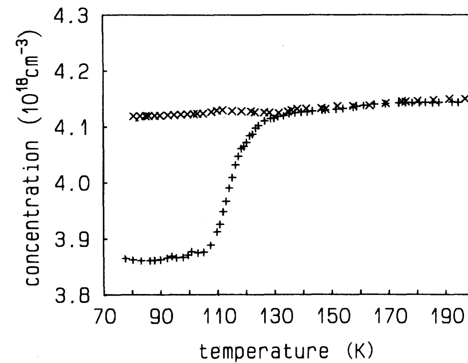


FIG. 2. Electron concentration measured at $p=0$ kbar during heating of the sample (GaAs:Si) in a metastable state (+). Decrease of the electron concentration was induced by pressure freezeout (cooling at $p=14.2$ kbar). The upper part of the figure illustrates the temperature dependence of the electron concentration measured after cooling sample at atmospheric pressure (×).

on carrier concentration, e.g., mobility. Knowledge of T_{min} and T_{max} is necessary for a proper interpretation of the low-temperature experimental results obtained by means of cooling the sample under pressure. This observation applies specially to measurements of the Hall coefficient versus pressure, which were used for determination of the energetic position of the localized donor state, E_{DX}. At $T < T_{min}$ occupation of DX centers becomes settled and metastable. Therefore, one should remember that all calculations which are based on the equilibrium statistics of the DX-state occupancy should be performed for $T > T_{max}$.

In the case of the HPFO procedure applied to n-GaAs samples for which the localized state of the donor impurity DX is degenerate with the conduction band (for all values of applied pressures), the barrier for electron emission from DX states to the conduction band determines the temperature transients of carrier concentration. Transport of electrons over the barrier E_E occurs between T_{min} and T_{max} (Fig. 2).

To estimate the value of these characteristic temperatures and to deduce the pressure dependence of E_E the temperature transients of R_H were measured for various metastable occupations of the localized state induced by HPFO. The obtained result (Fig. 3) shows that in the bulk sample of GaAs:Si and up to 10 kbar T_{min} and T_{max} seem to be weakly pressure dependent, or not pressure dependent at all. One can use this observation to interpret qualitatively changes of E_E with pressure. The measured time dependence of the electron concentration in the conduction band dn/dt depends on the rate of carrier emission from the DX center v_E in the following way:

$$\frac{dn}{dt} = v_E(N_D - n) , \tag{1}$$

where $N_D - n$ corresponds to the number of electrons captured by DX centers and N_D represents a concentra-

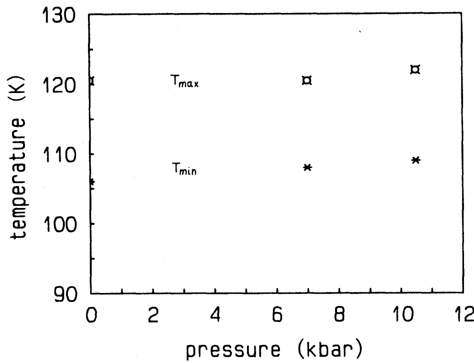


FIG. 3. Pressure dependence of T_{min} and T_{max} obtained from the temperature transients of the carrier concentration. Metastable occupations of the localized state were induced by high-pressure freezeout (HPFO) at $p=14.2$ kbar.

tion of donors. v_E is a thermally activated emission coefficient (for the emission of electrons to the conduction band[18])

$$v_E \propto \exp\left[-\frac{E_E}{kT}\right] . \quad (2)$$

From these two expressions one can see that at constant temperature the rate of electron transfer from DX centers to the conduction band decreases with increasing of the barrier height for electron emission E_E. Very weak pressure dependence of T_{min} and T_{max} in the examined sample of GaAs:Si reflects a weak sensitivity of E_E on pressure (a rate of temperature increase after every HPFO cycle was similar).

As is known from different papers and will be demonstrated below, the pressure shift of E_{DX} with respect to the Γ conduction band is significant and achieves a magnitude of from about -10 meV/kbar to more negative values.[22,32,33] Taking additionally into account (i) that $E_{DX}=E_C-E_E$ and (ii) that E_E is practically independent of applied pressure, it implies a decrease of E_C with increasing pressure [a significant sensitivity of E_C on pressure was reported for $Al_{1-x}Ga_xAs$:Si ($0.20<x<0.40$), Ref. 34]. This situation causes a corresponding modification of the configuration-coordinate diagram. The parabola of the CCD corresponding to the localized state of DX moves with pressure not only vertically but also horizontally. It produces effectively the inclined shift of this parabola closer to the parabola describing electrons in the conduction band (Fig. 4). This variation of the CCD reflects the decrease of the electron-lattice coupling strength for Si localized state in GaAs.

There is a corresponding result for the heterostructure of $GaAs/Al_xGa_{1-x}As$ (Ref. 31) where for pressures up to 7 kbar no T_{min} and T_{max} dependence on pressure was found. Analysis of the latter result is not simple due to the fact that Si donors reside in $Al_{0.3}Ga_{0.7}As$ and E_{DX} is located in the forbidden gap of $Al_xGa_{1-x}As$. It appears here that the characteristic temperatures become a complicated function of E_C and E_E.

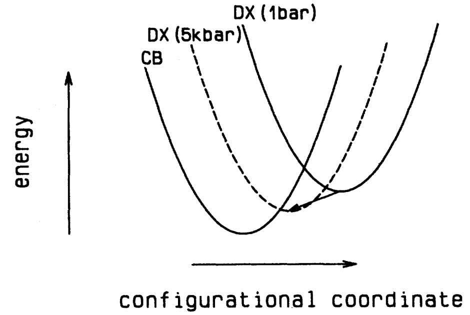


FIG. 4. Modification of the configuration-coordinate diagram with pressure for GaAs:Si.

In contrast, measurements of the characteristic temperatures T_{min} and T_{max} in epilayers of GaAs:O (Ref. 26) showed a significant increase of both temperatures with pressure ($dT_m/dp=1$ K kbar^{-1}).

B. Character of donor impurity in GaAs and determination of E_{DX}

In the Introduction we briefly discussed two models of donor which are intended to describe the nature of the DX center. However, for the purpose of clarity more detailed consideration of the alternative states of donor is required. For low dopant concentrations the positively charged state of donor $\mathscr{d}^+$ represents a fourfold-coordinated substitutional donor without deformation of its neighbor ions. In addition, due to its attractive potential, $\mathscr{d}^+$ can bind an electron and then it represents a shallow, hydrogeniclike state $\mathscr{d}^0$. These states form an impurity band separated from the conduction band and in the consequence a low-temperature deep-level transient[24] spectroscopy (DLTS) peak and $1s$-$2p$ transitions in the far-infrared absorption[19] have been observed. Thermal activation energy of the hydrogeniclike state (with respect to the Γ conduction band) for GaAs and $Al_{1-x}Ga_xAs$ with small x is about 5 meV. It is also possible that at certain conditions (e.g., applied pressure of about 30 kbar) $\mathscr{d}^+$ can bind an electron and form the localized state accompanied by LRE, DX^0. For higher concentration of donors (above about 1×10^{17} cm^{-3}) the impurity band related to $\mathscr{d}^0$ state merges into the conduction band. Electron states previously bound now become extended. The screening of $\mathscr{d}^+$-center potential is efficient enough to prevent localization of electrons on the hydrogeniclike orbitals. The sample used in the measurements performed here represent the latter case.

The localization of electrons is related to transformation of $\mathscr{d}^+$ centers to the deep DX states exhibiting lattice relaxation effects around them. Two possible versions of the DX center were mentioned previously. The appearance of the neutral, deep state DX^0 as the effect of the electron capture by $\mathscr{d}^+$ illustrates the first model. In the case of the second model where negatively charged state with LRE is related to electron localization we will limit our consideration to the situation described by the

reaction: $d^+ + 2e^- = DX^-$ (neglecting, e.g., the possibility of the neutral state without or with LRE formation as an intermediate step). Gain in energy resulting from LRE overcomes the energetic cost of accommodation of two electrons on one donor. This is an important implication of the "negative U" center concept.[20,21]

Room-temperature measurements reveal a strong increase of R_H at high pressures for the used samples. The only exception to this behavior has been found for the sample of GaAs:Te ($n = 7\times10^{18}$ cm^{-3}). R_H variation with pressure for the latter sample is similar to this observed for $n < 1\times10^{18}$ cm^{-3} and results from the electron transfer to the L and X subsidiary minima of the conduction band. Usually, the detected increase of R_H for more heavy doped samples occurs above certain critical pressure when donors start to capture electrons. Magnitude of this critical pressure decreases with increasing n. The same variation of R_H has been observed for samples consisting of epitaxially grown layers of the oxygen- and silicon-doped GaAs.[26,22] Figure 5 shows the dependence of the Hall concentration of carriers versus pressure for one of the bulk GaAs:Si samples ($n = 3.3\times10^{18}$ cm^{-3}) as compared with epitaxially grown sample of GaAs:Si ($n = 5.2\times10^{18}$ cm^{-3}).[22]

The observed behavior of R_H can be used for the determination of the energetic position of the deep donor level, E_{DX}. For this purpose the real number of electrons captured by DX centers has to be known. Moreover, since the electron distribution involves all three conduction-band minima Γ, L, and X (important as carrier concentration and pressure increase) the measured R_H is a complicated function of the electron concentration and their mobilities in the three bands as well as of the applied pressure. To determine contributions of n_Γ, n_L, and n_X to the total electron concentration n, the similar procedure and the parameters of the band structure to those proposed by Lifshitz *et al.*[32] were used. An effect of nonparabolicity has been taken into account (three-band model). We have assumed that at room temperature and

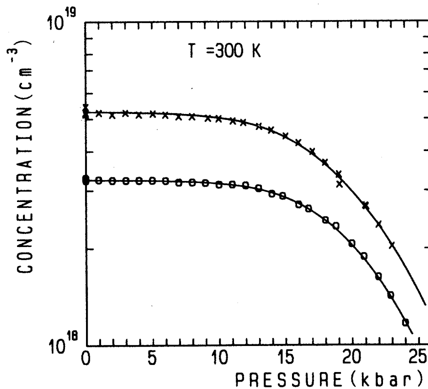
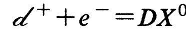


FIG. 5. Pressure dependence of the Hall concentration of electrons for GaAs:Si; $*$ denote the epitaxial layer, ○ denotes the bulk sample, solid line —— denotes the calculations (for explanations see text).

for n from the used range of carrier concentration all donors represent ionized, positively charged impurities, d^+. However, as was mentioned previously the two models of the deep states can be considered.

(1) With applied pressure it becomes energetically favorable to create a neutral state DX^0. Electron capture is represented by the reaction



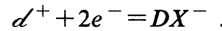
$$d^+ + e^- = DX^0$$

and the relation between the position of the E_{DX^0} level and electron concentation is given by

$$n = N_D \frac{\frac{1}{2}\exp\left[-\eta - \frac{E_1}{kT}\right]}{1+\frac{1}{2}\exp\left[-\eta-\frac{E_1}{kT}\right]} - N_A , \quad (3)$$

where N_D and N_A are the concentrations of donor and acceptor impurities, respectively, η is the reduced Fermi energy, and E_1 represents the energy required to promote an electron from the DX^0 state to the conduction band.

(2) Application of pressure leads to the formation of the localized states which trap two electrons each. The respective reaction may be expressed as follows:



$$d^+ + 2e^- = DX^- .$$

It was argued by Chadi and Chang[21] and Khachaturian *et al.*[20] that formation of the neutral DX^0 state became, in this situation, energetically unfavorable. At the same time for the highly doped samples used in this work the binding of electrons by the Coulomb potential of d^+ centers is unlikely. Therefore, capture of all carriers on DX^- centers implies that half of an ionized, substitutional donor d^+ remains unoccupied. We use the following formula to relate n and E_{DX^-} (see Appendix):

$$n = N_D \frac{1-\exp\left[2\eta + \frac{E_2}{kT}\right]}{1+\exp\left[2\eta+\frac{E_2}{kT}\right]} - N_A , \quad (4)$$

where E_2 is the energy required to promote two electrons captured on DX^- center to the conduction band. Formulas (3) and (4) enable a determination of E_{DX} at 300 K and at pressures for which the deep state captures electrons. We have computed E_{DX} under the assumption $N_D \gg N_A$. Pressure dependence of E_{DX^0} and E_{DX^-} as well as the edges of L and X conduction bands for one of the samples is shown in Figs. 6(a) and 6(b), respectively. Linear extrapolation of E_{DX} to its eventual position at ambient pressures gives values of the pressure coefficient dE_{DX}/dp and E_{DX}(1 bar). The applied pressure causes the shift of E_{DX} down to the Fermi level. However, for the used dopant concentrations and pressures the DX state remains resonant with the conduction band. The important result extracted from this analysis consists of the observation that the variation of E_{DX^0} and E_{DX^-} with pressure at 300 K is different from the shift of the L con-

duction band. The large magnitude of E_{DX}(1 bar) exceeds significantly the value $E_{DX} \simeq 170$ meV resulting from the extrapolation from $Al_xGa_{1-x}As$ as well as $E_{DX} \simeq 280$ meV obtained by Theis *et al.*[24] (within model 1) for highly doped samples.

Then we have calculated changes of the Hall concentration of electrons with pressure. For this purpose a linear variation of E_{DX} with pressure was assumed. Though a satisfactory agreement between the experimental and calculated dependences for the both models (1) and (2) was obtained, taking into account a lowering of the Γ conduction-band edge (from 10 to 20 meV) for the samples with the highest dopant concentration enabled to improve this agreement (Fig. 5). Results of calculations for the used samples are summarized in Table I. For the purpose of illustrating the application of the concept of a DX^- center, values of E_{DX^-} for these samples of GaAs:Si are given in the table.

To proceed further with examination of the localized *DX* center behavior, the measurements of R_H variation with pressure at 77 and 4.2 K were performed (Fig. 7). The experimental procedure consisted of cooling of the

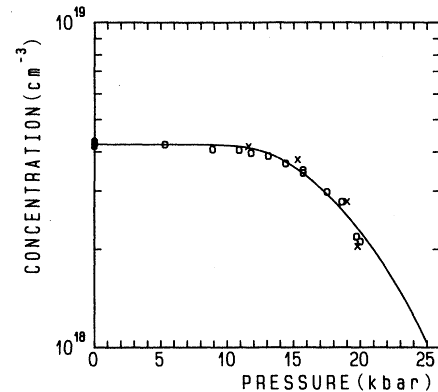


FIG. 7. Pressure dependence of the Hall concentration of electrons for GaAs:Si measured at 77 K (○) and 4.2 K (×), the solid line illustrates calculations based on equilibrium statistics of the *DX* level occupancy and performed at $T = 120$ K.

samples under pressure applied at 300 K. Variation of R_H with pressure at low temperatures is similar to this dependence detected at 300 K. Due to the metastability effect, the results for both temperatures are similar (car-

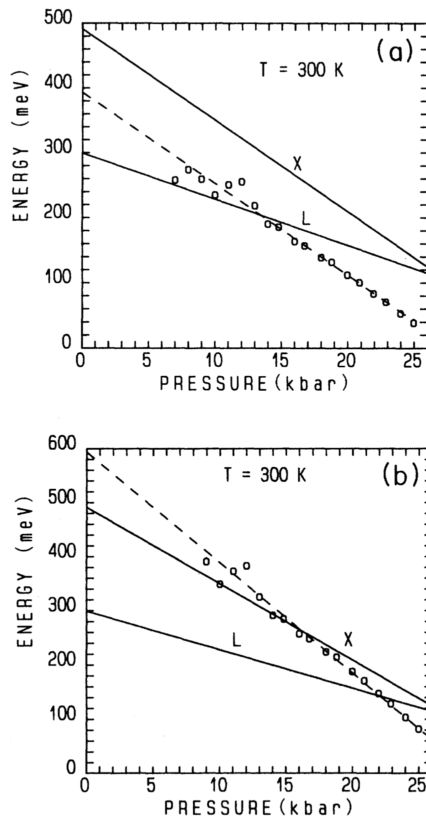


FIG. 6. GaAs:Si ($n = 3.2 \times 10^{18}$ cm^{-3}). Pressure dependence of *L* and *X* conduction-band minima (solid lines) and *DX* level position (dashed line) with respect to the bottom of Γ band. Open circles represent the calculations (data taken from Fig. 5); (a) calculations performed within the model of DX^0 state, (b) and within the model of DX^- state.

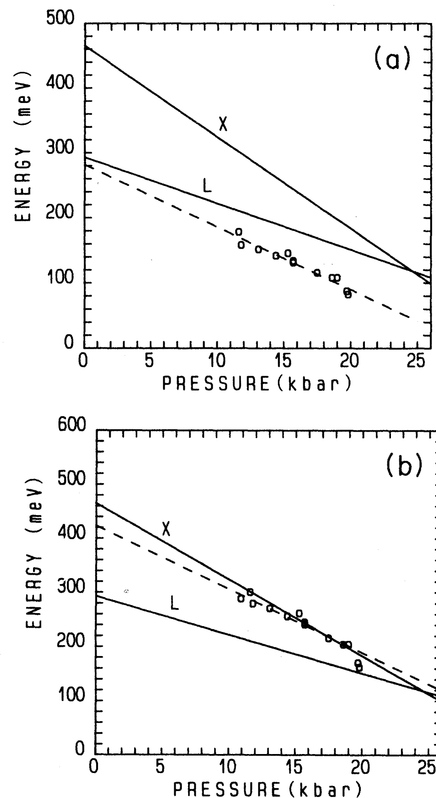


FIG. 8. Pressure dependence of *L* and *X* conduction-band minima (solid lines) and *DX* level position (dashed line) with respect to the bottom of the Γ band. Open circles represent the calculations (data taken from Fig. 7): (a) calculations performed within the model of DX^0 state, and (b) within the model of DX^- state.

rier concentration was settled at $T > 110$ K). Thus the same procedure for determination of E_{DX} and dE_{DX}/dp could be applied here except for the fact that calculations are related to the temperature $T \approx T_{\min}$. We found lower values of both $E_{DX}(p)$ and dE_{DX}/dp (for $T = 120$ K) in comparison with their respective counterparts obtained for $T = 300$ K within two models of localized DX state [Table I and Figs. 8(a) and 8(b)]. The assumption about the one-electron capture and formation of the DX^0 center implies the shift of E_{DX} with pressure which accidentally may appear to be similar to the one characterizing pressure dependence of the L conduction band. Moreover, linear extrapolation of the DX level position to its value E_{DX}(1 bar) gave the thermal activation energy about 300 meV (above the bottom of Γ conduction band). This value is consistent with the result of Theis *et al.*,[24] $E_{DX} \simeq 280$ meV, obtained within the same model for samples with higher doping level (at ambient pressure and at $T \simeq 150$ K).

The important results of the performed studies lead to the following conclusion about the nature of the DX center. It represents the localized electronic state coupled with the crystal lattice and its wave function should be composed of a wider region of the Brillouin-zone contributions than one minimum of the conduction band only. The temperature dependence of both E_{DX} and dE_{DX}/dp results from the performed studies.

C. Mobility

Pressure variation of electron mobility measured at 77 and 4.2 K in the used samples consists of two regions (Fig. 9). μ decreases with increasing pressure while the carrier concentration remains constant. Then, an increase of μ appears which reflects the respective decrease in the electron density (Fig. 7). A similar tendency was reported for epitaxially grown samples of GaAs:Si, GaAs:Sn[33] and GaAs:O.[26] What are the effects contributing to the observed behavior? Within the Born approximation and for the strong degeneracy case the scattering by (screened) ionized impurities is given by[36]

$$\mu = \frac{3\pi^2 \epsilon^2 \hbar^3}{e^2} \frac{n}{N_i} \frac{1}{m_e(k_F)^2} \frac{1}{F(\lambda, k_F)} , \qquad (5)$$

where ϵ and N_i are the dielectric constant and concentration of the ionized impurities, respectively. $m_e(k_F)$ is the conductivity effective mass, evaluated at the Fermi surface. $F(\lambda, k_F)$ is the scattering function[36] and λ^{-1} represents the Thomas-Fermi screening length. In the region where applying pressure does not change n the respective increase of the effective mass (with increasing energy gap) and pressure-induced changes of the dielectric constant[37] imply the observed decrease of the electron mobility (the solid, straight line on the left side of Fig. 9). Then due to the decrease in the carrier density, k_F and thus m_e decrease. The same occurs for the scattering function F. All these changes imply an increase of μ.

Contribution to μ originating in the changes of free-carrier density can be discussed within the introduced models of the DX center, (1) and (2). In the case (1) decrease in the carrier concentration results from the capture of electrons by d^+ states. As a result neutral, localized DX^0 states appear. Consequently, concentrations of N_i and n decrease with pressure with the same rate (if compensation effect is neglected), therefore the second term in Eq. (5) should remain equal to 1. The positive slope of the calculated mobility variation for higher pressure values reflects this situation (Fig. 9).

If the situation is consistent with model (2) the process of two-electron capture by the d^+ center (which implies formation of the DX^- state) does not change the number of charged defects in the sample. It results in inducing a significant decrease of μ, which gives the contribution overcompensating the influence of terms which lead to the rise of mobility examined for the model of the DX^0 center. Finally, for the model of the DX^- center one obtains an additional decrease of mobility after trapping of carriers onto deep states.

Comparison of the above qualitative analysis with the experimental results leads to the conclusion that the DX^0 center is more likely to form than the DX^- state. This distinguishes model (1) as properly describing a process of electron capture by the d^+ state of a donor. There is, however, one other hypothetical situation which may favor model (2). For highly doped samples of n-type GaAs one can assume that some gain in energy would appear if the process of d^+ conversion to DX^- results in creation of pairs d^+DX^-. Thus the deep localized state would appear at the donor place close to the d^+ center. This situation implies a charge compensation of d^+ and DX^- states and consequently it reduces an efficiency of the ionized impurity scattering. An electron situated far away from the pairs of d^+d^+ and d^+DX^- is subject to substantially different scattering potentials.

In contrast to the results on relations between electron mobility and carrier concentration presented above stand the unpublished data of Low and Costa as well as those of Theis cited by Khachaturian *et al.*[20] Namely, an in-

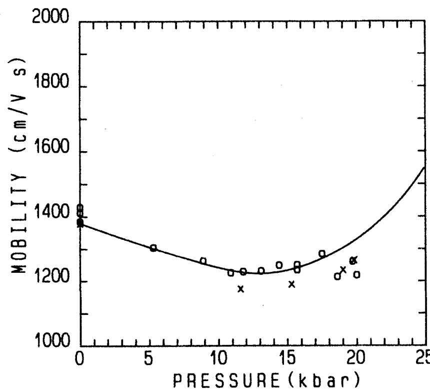


FIG. 9. Electron mobility vs pressure for GaAs:Si ($n = 4.2 \times 10^{18}$ cm^{-3}); the solid line corresponds to the relative changes of mobility (theory for DX^0 center), experimental points represent measurements performed at 77 K (○) and at 4.2 K (×).

crease in Hall mobility has been observed after photoionization of the DX center (i.e., with increasing electron concentration). This observation was used as an argument supporting the idea of DX^--center formation. In our opinion the final conclusion concerning the problem of compliance between the behavior of electron mobility and one of the considered models of the localized DX center can be drawn only after detailed analysis followed by proper calculations.

At this point it seems to be worthwhile to mention the idea of Mycielski[38] who proposed a formation of a superlattice of Fe^{3+} ionized donors in highly doped HgSe:Fe. Minimization of the screened Coulomb interactions between Fe^{3+} ions might cause (at low temperatures) the correlations in their arrangement between neutral Fe^{2+} (the tendency in the positions of Fe^{3+} to be rather distant from each other). A correlation of scatterers enabled us to explain a dramatic increase in mobility observed for HgSe:Fe in the range where both Fe^{3+} and Fe^{2+} were present (n 5×10^{18} cm^{-3}). Applying this proposal to GaAs:Si (Ref. 39) is related to the situation where d^+ and DX^0 are present. Therefore, even within model (1) the increase in mobility with increase in the carrier number could be explained qualitatively.

IV. CONCLUSIONS

The main purpose of this paper was to determine the energetic position, E_{DX}, of the localized state of the DX center as well as its pressure dependence, dE_{DX}/dp, in bulk, heavily doped n-GaAs. Two approaches to the DX center were applied here.

(i) The DX^0 center represents a neutral donor which appears in GaAs after a capture of one electron by the ionized, substitutional donor, i.e., the d^+ center. In this situation E_{DX^0} represents the energy required to promote one electron from the DX^0 state to the conduction band.

(ii) The DX^- center, which is formed after the trapping of two electrons by the d^+ center. E_{DX^-} is the energy of promoting two electrons from the DX^- localized state to the conduction band.

These two models of the DX center lead to the following important conclusions. Variation of E_{DX} with pressure at 300 K is different from the shift of the L conduction band. For the samples from the used dopant concentration range dE_{DX^0}/dp resembles more pressure variation of the X conduction band. dE_{DX^-}/dp is slightly smaller than twice the value of dE_{DX^0}/dp. Linear extrapolation of the DX level position to its eventual location at ambient pressures gives values in the range of 0.4–0.45 eV for E_{DX^0} and much higher values for E_{DX^-} (with respect to the Γ minimum of the conduction band).

E_{DX} and dE_{DX}/dp exhibit a decrease with lowering temperature. E_{DX^0} (1 bar) is found to be located approximately 0.25–0.3 eV above the Γ conduction band. The latter result is very similar to the one obtained by Theis *et al.*[24] for epitaxially grown samples of GaAs with $n>5\times10^{18}$ cm^{-3}.

Summarizing the part of the paper devoted to the studies of the energetic position of E_{DX} and its pressure dependence, it is possible to conclude that the DX center represents the localized electronic state coupled to the crystal lattice. Its wave function should be composed of the wide range of the Brillouin-zone contribution and we believe that it is incorrect to associate the DX center with any minimum of the conduction band. The important result consists of finding the temperature dependence of both E_{DX} and dE_{DX}/dp.

The performed measurements enable us to study the pressure dependence of the configuration-coordinate diagram for GaAs:Si. Weak sensitivity of the barrier for carrier emission from the DX state to the conduction band is deduced. It implies a weakening of the coupling between the electronic subsystem of the Si donor and the surrounding crystal lattice as the result of applying pressure. There is evidence[26] that the GaAs crystal doped with O behaves differently. Namely, the barrier E_E exhibits much higher sensitivity to applied pressure. It might be evidence of the different chemical nature of Si and O impurities.

Analysis of how the electron mobility changes with pressure shows that for the bulk samples with carrier concentration between 2×10^{18} and 5×10^{18} cm^{-3} μ tends to increase with decreasing carrier concentration. The simplified, qualitative analysis of the mobility variation with density of carriers can lead to various results, especially when some tendencies to correlations in the donor distribution are assumed.

Both observed effects—the increase of μ with rising the carrier concentration (this work and Refs. 26 and 33) as well as the opposite behavior[20]—might result from consideration of DX^- or DX^0 concepts, respectively. However, speculations taking into account the proposed appearance of the ordered superlattice of d^+ centers (within the statistically distributed DX^0 states) or pairs of d^+DX^- centers can be applied for the same purpose. Thus, these considerations show that as long as the results of proper calculations are not available it is difficult to use the data on electron mobility in GaAs for the ultimate choice between one of the two proposed models of the DX center, i.e., DX^0 and DX^-.

ACKNOWLEDGMENTS

The authors are grateful to Professor J. Baranowski, Dr. J. Kossut, and Dr. T. Dietl for stimulating discussions. We thank Dr. L. Zanotti for supplying a part of the samples used. This work was supported by the Central Program of Fundamental Research No. CPBP-01-5 of the Polish Ministry of Science, Higher Education and Technology.

APPENDIX: DX^- STATISTICS

To begin we will consider a situation when the donor impurity with several charge states can be found in a semiconductor.[40] The ratio of the occupation of the two charge states which differ in a number of bound electrons is given in equilibrium by

$$\frac{N_{r-1}}{N_r}=\frac{g_{r-1}}{g_r}\exp\left[\eta+\frac{E_{r-1,r}}{kT}\right], \tag{A1}$$

where η is the reduced Fermi energy, index r corresponds to the number of electrons lost from the donor, $E_{r-1,r}$ represents the binding energy required for one electron to be promoted from the donor in the state $(r-i)$, and g stands for the degeneracy factor.

For a lightly doped GaAs crystal and according to the concept of the negatively charged donor center,[21] there are three possible states of donor. Namely, $\mathcal{d}^+$ a positively charged center with electron excited to the conduction band (with density $N_{\mathcal{d}^+}$), $\mathcal{d}^0$, a neutral, substitutional center, with one electron bound on a hydrogeniclike orbit (with density $N_{\mathcal{d}^0}$), and DX^-, negatively charged, highly localized center with two electrons captured and exhibiting lattice relaxation effects (density N_{DX^-}). This situation implies the following dependences:

$$\frac{N_{\mathcal{d}^0}}{N_{\mathcal{d}^+}}=\frac{g_0}{g_+}\exp\left[\eta+\frac{E_0}{kT}\right], \quad \text{(A2)}$$

where E_0 is the energy of the hydrogenic state of donor,

$$\frac{N_{DX^-}}{N_{\mathcal{d}^0}}=\frac{g_-}{g_0}\exp\left[\eta+\frac{E_{DX^-}}{kT}\right]. \quad \text{(A3)}$$

Ionization of the center binding two electrons, i.e., transformation from the DX^- state to a $\mathcal{d}^+$ state, requires supplying the energy $E_2=E_{DX^-}+E_0$. The ratio of the occupation of DX^- and $\mathcal{d}^+$ states is given by

$$\frac{N_{DX^-}}{N_{\mathcal{d}^+}}=\frac{g_-}{g_+}\exp\left[2\eta+\frac{E_2}{kT}\right]. \quad \text{(A4)}$$

The concentration of electrons in the conduction band (given by the neutrality equation) is

$$n=N_{\mathcal{d}^+}=N_{DX^-}-N_A , \quad \text{(A5)}$$

where N_A represents the acceptor concentration.

In the case of highly doped samples which is considered in this paper, there are no electrons bound on the hydrogenic states (concentration of impurities are above the critical one for the Mott transition). Thus the total concentration of donors, N_D, is given by

$$N_D=N_{\mathcal{d}^+}+N_{DX^-}=N_{\mathcal{d}^+}\left[1+\frac{N_{DX^-}}{N_{\mathcal{d}^+}}\right] \quad \text{(A6)}$$

then

$$N_{\mathcal{d}^+}=\frac{N_D}{1+N_{DX^-}/N_{\mathcal{d}^+}} . \quad \text{(A7)}$$

We have from (A5)

$$n=N_{\mathcal{d}^+}\left[1-\frac{N_{DX^-}}{N_{\mathcal{d}^+}}\right]-N_A \quad \text{(A8)}$$

and using (A7)

$$n=N_D\frac{1-N_{DX^-}/N_{\mathcal{d}^+}}{1+N_{DX^-}/N_{\mathcal{d}^+}}-N_A . \quad \text{(A9)}$$

Since $g_+=g_-=1$ we have

$$n=N_D\frac{1-\exp(2\eta+E_2/kT)}{1+\exp(2\eta+E_2/kT)}-N_A , \quad \text{(A10)}$$

where E_2 is the energy required to promote two electrons captured on the DX^- center to the conduction band.

[1] M. I. Nathan, Solid-State Electron. **29**, 167 (1986).
[2] S. Porowski and W. Trzeciakowski, Phys. Status Solidi B **128**, 11 (1985).
[3] G. A. Baraff, in *Proceedings of the 14th International Conference on Defects in Semiconductors,* edited by H. J. von Bardeleben (Trans Tech, Aedermansdorf, 1986), p. 377.
[4] M. Baj, L. Dmowski, M. Konczykowski, and S. Porowski, Phys. Status Solidi A **33**, 421 (1976).
[5] J. M. Langer, in *New Developments in Semiconductors,* Vol. 122 of *Lecture Notes in Physics,* edited by F. Beleznay, G. Ferenci, and J. Giber (Springer-Verlag, Berlin, 1980), p. 123.
[6] C. M. Penchina, A. Klein, and K. Weiser, J. Phys. Soc. Jpn. Suppl. A **49**, 287 (1980).
[7] T. Suski, P. Wisiniewski, L. Dmowski, G. Grabecki, and T. Dietl, J. Appl. Phys. **65**, 1203 (1989).
[8] S. Porowski, M. Konczykowski, and J. Chroboczek, Phys. Status Solidi B **63**, 291 (1974).
[9] L. Dmowski, M. Baj, P. Ioannides, and R. Piotrzkowski, Phys. Rev. B **26**, 4495 (1982).
[10] L. Dmowski, M. Baj, M. Kubalski, R. Piotrzkowski, and S. Porowski, in *Proceedings of the 14th International Conference on Semiconductor Physics,* IOP Conf. Proc. No. 43, edited by B. L. H. Wilson (IOP, Bristol, 1979), p. 417.
[11] L. Konczewicz, E. Litwin-Staszewska, S. Porowski, A. Iller, R. L. Aulombard, J. L. Robert, and A. Joullie, in *Proceedings of the 16th International Conference on the Physics of Semiconductors, Montpellier, 1982,* edited by M. Averous (North-Holland, Amsterdam, 1983).
[12] G. A. Baraff, in *Proceedings of the 19th International Conference on the Physics of Semiconductors, Warsaw, 1988,* edited by W. Zawadzki (The Institute of Physics/Polish Academy of Sciences, Warsaw, 1988), p. 359.
[13] P. Dreszer and M. Baj, *Proceedings of the 15th International Conference on Defects in Semiconductors,* edited by G. Ferenczi (Trans Tech, Aedermansdorf, 1989), p. 101.
[14] D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).
[15] T. N. Morgan, Phys. Rev. B **34**, 2664 (1986).
[16] J. C. M. Henning and J. P. M. Ansems, Semicond. Sci. Technol. **2**, 1 (1987).
[17] H. P. Hjalmarson and T. J. Drummond, Phys. Rev. Lett. **60**, 2410 (1988); J. E. Dmochowski, J. M. Langer, J. Raczynska, and W. Jantsch, Phys. Rev. B **38**, 3276 (1988).
[18] See, also the review by D. V. Lang, in *Deep Centers in Semiconductors, edited by S. T. Pantelides* (Gordon and Breach, New York, 1986), p. 489.
[19] T. N. Theis, T. F. Kuech, L. F. Palmateer, and P. M. Mooney, Inst. Phys. Conf. Ser. No. 74, edited by B. de Cremoux (IOP, Bristol, 1984), p. 241.
[20] K. Khachaturyan, E. R. Weber, and M. Kaminska, Lawrence Berkeley Laboratory Report LBL-24994, March 1988 (un-

published).
[21]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
[22]T. Suski, E. Litwin-Staszewska, R. Piotrzkowski, P. Wisniewski, L. Dmowski, L. Zanotti, Xiao Tang, and L. J. Gilling, in Ref. 12, p. 1047.
[23]M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Omi, and S. Minomura, Jpn. J. Appl. Phys. **24**, L893 (1985).
[24]T. N. Theis, P. M. Mooney, and S. L. Wright, Phys. Rev. Lett. **60**, 361 (1988).
[25]P. M. Mooney, G. A. Northrop, T. N. Morgan, and H. G. Grimmeiss, Phys. Rev. B **37**, 8298 (1988); M. F. Li, P. Y. Yu, E. R. Weber, and W. Hansen, *ibid.* **36**, 4531 (1987).
[26]L. Dmowski, D. Wasik, E. Litwin-Staszewska, T. Suski, P. Wiśniewski, and W. H. Zhuang, in Ref. 13, p. 493.
[27]N. Chand, T. Henderson, J. Klem, W. T. Masselink, R. Fischer, Y. C. Chang, and H. Morkoc, Phys. Rev. B **30**, 4481 (1984).
[28]L. X. He, K. P. Martin, and R. J. Higgins, Phys. Rev. B **36**, 6508 (1987).
[29]D. E. Theodorou and H. J. Queisser, Appl. Phys. **23**, 121 (1980).
[30]E. Calleja, A. Gomez, E. Munoz, and P. Camara, Appl. Phys. Lett. **52**, 1877 (1988); P. M. Mooney, T. N. Theis, and S. L. Wright, in Ref. 13, p. 1109; J. Kaniewski, M. Kaniewska, and K. Zdansky, J. Appl. Phys. **62**, 4634 (1987).
[31]T. Suski, E. Litwin-Staszewska, P. Wiśniewski, L. Dmowski, W. H. Zhuang, G. B. Liang, D. Z. Sun, and Y. P. Zhen, J. Appl. Phys. **63**, 2307 (1988); R. Piotrzkowski, J. L. Robert, E. Litwin-Staszewska, and J. P. Andre, Phys. Rev. B **37**, 1031 (1988).
[32]N. Liftshitz, A. Jayaraman, R. A. Logan, and H. C. Card, Phys. Rev. B **21**, 670 (1980).
[33]D. K. Maude, J. C. Portal, L. Dmowski, T. Foster, L. Eaves, M. Nathan, M. Heiblum, J. J. Harris, and R. B. Beall, Phys. Rev. Lett. **59**, 815 (1987).
[34]P. M. Mooney, E. Calleja, S. L. Wright, and M. Heiblum, in *Defects in Semiconductors,* edited by H. J. von Bardeleben (Trans Tech, Switzerland, 1986), p. 417.
[35]M. O. Watanabe, K. Morizuka, M. Mashita, Y. Ashizawa, and Y. Zohta, Jpn. J. Appl. Phys. **23**, L103 (1984).
[36]W. Zawadzki, in *Handbook of Semiconductors,* edited by W. Paul (North-Holland, Amsterdam, 1982), Vol. 1, p. 725.
[37]Z. Wasilewski and R. A. Stradling, Semicond. Sci. Technol. **1**, 264 (1986).
[38]J. Mycielski, Solid State Commun. **60**, 165 (1986); W. Dobrowolski, K. Dybko, C. Skierbiszewski, T. Suski, E. Litwin-Staszewska, S. Miotkowska, J. Kossut, and A. Mycielski, in Ref. 12, p. 1247.
[39]T. Dietl, L. Dmowski, J. Kossut, E. Litwin-Staszewska, R. Piotrzkowski, T. Suski, K. Światek, and Z. Wilamowski, in Proceedings of the 17th International School of Physics of Semiconducting Compounds, Jaszowiec, 1989 [Acta. Phys. Polon. (to be published)].
[40]J. S. Blakemore, *Semiconductor Statistics* (Pergamon, Oxford, 1962).