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$Co^{1+}(3d^8)$ double acceptor state in GaAs

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Hall-effect and resistivity measurements were performed on *n*-type GaAs:Co samples under hydrostatic pressure up to 1.3 GPa at 300 and 77 K. The experimental results revealed the existence of the $Co^{1+}(3d^8)$ double acceptor state, degenerate with the conduction band (as far as the thermal ionization is concerned). Comparison of the experimental data with the calculated pressure variations of the Hall coefficient and the Hall mobility allowed determination of the energy of the Co^{2+}/Co^{1+} level and its pressure and temperature dependences. Moreover, it turned out that the Co^{2+}/Co^{1+} level density of states has the form of a broadened distribution of width in the order of 10^{-2} eV.

I. INTRODUCTION

Transition metals (TM's) substituting cation atoms in II-VI and III-V semiconducting compounds create deep (highly localized) impurity states. In III-V compounds (e.g., GaAs) a TM impurity gives three electrons to the bonds and thus the neutral charge state A^0 corresponds to the $M^{3+}(3d^n)$ ion configuration, the single ionized acceptor A^- to the $M^{2+}(3d^{n+1})$ state and the double acceptor state A^{2-} to the $M^{1+}(3d^{n+2})$ state. Positions of all the experimentally observed fundamental levels given by the different charge states of TM impurities in III-V compounds have been reported in Refs. 1, 2, and 3. In GaAs the energies of M^{3+}/M^{2+} levels have been experimentally determined for the following transition metals: V, Cr, Mn, Fe, Co, Ni, and Cu. However, the energetic position of M^{2+}/M^{1+} levels is known only for Cr and Ni. In GaAs:Co the fundamental $Co^{3+}(3d^6)/Co^{2+}(3d^7)$ acceptor level is of $^4A_2$ symmetry and lies at about 0.16 eV above the valence band.[4,5,6] Therefore, in *p*-type samples this level is empty, which corresponds to the $Co^{3+}(3d^6)$ neutral charge state. For a higher Fermi-level energy ($E_F > 0.16$ eV), the single ionized acceptor $Co^{2+}(3d^7)$ state can be observed either in EPR measurements[7,8] or in intraimpurity absorption measurements.[9,10,11] The Co^{2+} charge state can be easily detected in absorptionsmea urements due to the strong and sharp zero-phonon line (ZPL) at 11 317 cm^{-1} (1.403 eV) which originates from$^4A_2(F) \rightarrow {}^4T_1$ (P) intra-$3d^7$-subshell optical transition. Up to now, the double acceptor Co^{1+} charge state has never been observed in GaAs. However, the inspection of certain trends which exist for M^{3+}/M^{2+} levels in GaP and GaAs and for M^{2+}/M^{1+} levels in (GaP) (as well as for TM levels in II-VI compounds or for free TM ion $3d^{n+1} \rightarrow 3d^n4s$ excitation energies)[1,2,12] enables us to estimate the position of the Co^{2+}/Co^{1+} level in GaAs. Indeed, the energy of TM impurity levels decreases from light to heavier elements with a characteristic jump between the $3d^5$ electronic configuration (half-filled $3d$ subshell) and the $3d^6$ configuration. Assuming that the above trend should be reproduced in the case of M^{2+}/M^{1+} levels in GaAs and adopting the experimentally determined energies of Cr^{2+}/Cr^{1+},[13] and Ni^{2+}/Ni^{1+},[14] one can roughly estimate the position of the Co^{2+}/Co^{1+} level to be on the order of 100 meV above the conduction-band edge.

The idea of the present work was to search for the $Co^{1+}(3d^8)$ double acceptor state in highly doped *n*-type GaAs:Co samples by means of high hydrostatic pressure. Because the pressure coefficient of the Γ_6 conduction-band minimum should be considerably greater than that of the highly localized Co^{2+}/Co^{1+} impurity level, one can expect that the energy of the Co^{1+} state should decrease with pressure relative to the Γ_6 conduction-band edge. Thus, at sufficiently high pressures, some free electrons would be trapped on the Co^{2+}/Co^{1+} level, which could be easily detected in Hall measurements. This paper presents the results of Hall effect and electrical conductivity measurements performed on *n*-type GaAs:Co samples under high hydrostatic pressure which revealed the pressure induced activation of the Co^{1+} double acceptor state. Analysis of the experimental data enabled the determination of the Co^{2+}/Co^{1+} level energy and its pressure dependence. To our knowledge, this is the first observation of the Co^{2+}/Co^{1+} level in GaAs.

II. EXPERIMENTAL METHODS AND RESULTS

A. Preparation of samples

To prepare the investigated samples we used bulk *n*-type GaAs with an initial free-electron concentration of 4.5×10^{18} cm^{-3}. Cobalt impurities were introduced by evaporating a layer of pure Co metal onto a slice of semiconductor and then diffusing it at 1030–1080 K for about a day.[15] For the experiments we chose four Co-doped samples (hereafter denoted as Co2, . . . , Co5) with different Co concentrations and free-electron concentrations ranging from 2×10^{18} cm^{-3} to 4×10^{18} cm^{-3}. For the sake of comparison, we also used two Co-free samples (T1

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and T2) which are annealed in the same way as the other samples. Since both optical and transport measurements were required, the same samples were first optically polished with indium electrical contacts applied after completing the transmission experiments.

B. Optical measurements

Due to the strong ZPL connected with the $^4A_2(F) \rightarrow {}^4T_1(P)$ intra-$3d^7$-subshell optical transition,[10] the transmission measurements performed on n-type GaAs:Co samples enabled the determination of the relative concentration of Co^{2+} ions in the sample. Therefore, for all the investigated samples the transmission spectra in the range of the ZPL (i.e., near to 11 317 cm^{-1}) were measured at ambient pressure. We used a 0.4-m focal-length monochromator with a grating of 600 lines/mm and a S-20 EMI photomultiplier. The samples were immersed in liquid nitrogen, $T = 77$ K. The T1 and T2 test samples revealed no ZPL structure. The peak absorption of the ZPL (α), was greatest for the Co2 sample and equal to about $\alpha = 16$ cm^{-1}. Because of each crystal, α should be proportional to the Co^{2+} ion concentration (N), one can estimate the relative values:

$$N_i/N_0 = \alpha_i/\alpha_0 \,, \tag{1}$$

where the subscript i stands for Co3, Co4, or Co5, and $i = 0$ corresponds to the Co2 reference sample.

Table I gives the α_i/α_0 values together with the free-electron concentrations and mobilities measured for all the samples. It is clear that the electron mobility of Co-free samples is markedly higher than that of Co-doped ones. Moreover, for the latter samples, the higher the Co^{2+} content, the lower the free-electron concentration.

C. Transport measurements

The main part of our investigation consisted of Hall effect (weak magnetic field regime) and resistivity measurements performed under hydrostatic pressure up to 1.3 GPa at 77 and 300 K. The samples were placed in a Cu-Be high-pressure cell, using the helium gas as the pressure transmitting medium, which ensured that even at 77 K the pressure was fully hydrostatic.

The pressure variations of Hall coefficient and Hall mobility measured for all the samples are presented in Figs. 1–4. In Figs. 1 and 2 one can see that for all the Co-doped samples $1/eR_H$ decreases with pressure and then saturates. In the T1 and T2 test samples the free-electron concentration was pressure independent. The pressure dependencies of the Hall mobility are also much different for Co-doped and Co-free test samples. For the Co-doped samples a strong and nonlinear (especially at $T = 77$ K, see Fig. 4) decrease of $R_H\sigma$ upon pressure was observed. All of the above experimental results can be explained by the existence of the $Co^{1+}(3d^8)$ double acceptor state degenerate with the conduction band and being close to the Fermi level in the investigated samples. The qualitative interpretation is as follows. The Co^{2+}/Co^{1+} level is almost empty at ambient pressure and most of the Co ions are in the Co^{2+} charge state. As the pressure is increased the energy of the Co^{2+}/Co^{1+} level decreases relative to the Fermi energy, the free electrons are trapped, and the Co ions change their charge state via $Co^{2+}(A^-) + e^-_{CB} \rightarrow Co^{1+}(A^{2-})$, where e^-_{CB} signifies a conduction-band free electron. This results in the ob-

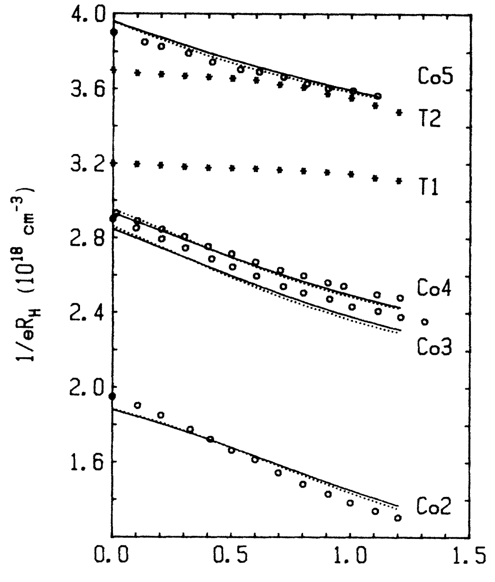

FIG. 1. The pressure variations of $1/eR_H$ measured at $T = 300$ K. Dotted lines were calculated for the δ-like Co^{1+} density of states while solid lines for the Gaussian-like one.

TABLE I. Experimental values of the free-electron concentration ($n_{77\,K}$) and mobility ($\mu_{77\,K}$), the pressure-induced relative change of the free-electron concentration ($\Delta n/\Delta n_0$), and the relative intensity of the Co^{2+} 11 317-cm^{-1} ZPL, measured at 77 K, for different GaAs samples; together with the fit values of the cobalt atom concentration (N_{Co}), the additional acceptor concentration (N_a) and the broadening parameter (Δ).

Sample	$n_{77\,K}$ (10^{18} cm^{-3})	$\mu_{77\,K}$ ($cm^2/V\,s$)	N_{Co} (10^{18} cm^{-3})	N_a (10^{18} cm^{-3})	Δ (meV)	$\frac{\Delta n}{\Delta n_0}$	$\frac{\alpha}{\alpha_0}$
Co2	2	1090	0.87	1.43	15	1	1
Co3	2.9	1000	0.87	0.31	20	0.55	0.56
Co4	3	1000	0.8	0.3	20	0.56	0.62
Co5	3.9	1100	0.69	0	20	0.18	0.16
T1	3.2	2000	0	1.3		0	0
T2	3.7	1600	0	0.8		0	0

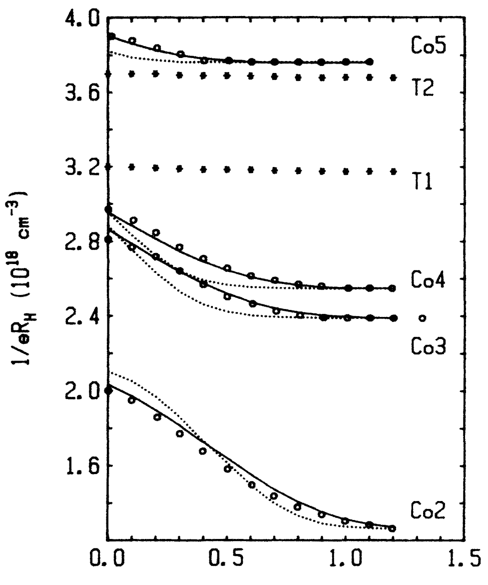

FIG. 2. The pressure variations of $1/eR_H$ measured at $T=77$ K. Dotted lines were calculated for the δ-like Co^{1+} density of states while solid lines for the Gaussian-like one.

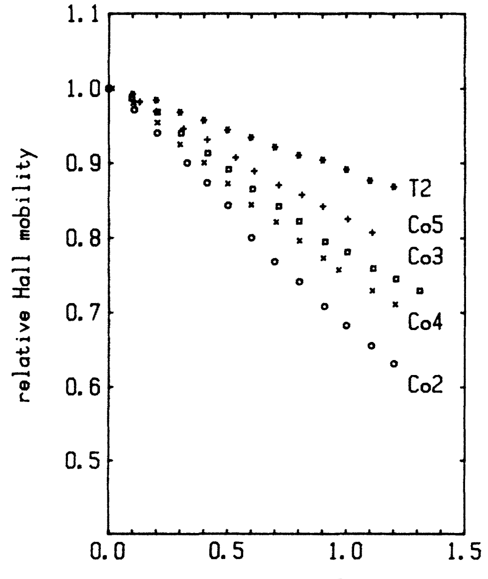

FIG. 3. The pressure variations of relative Hall mobility measured at $T=300$ K.

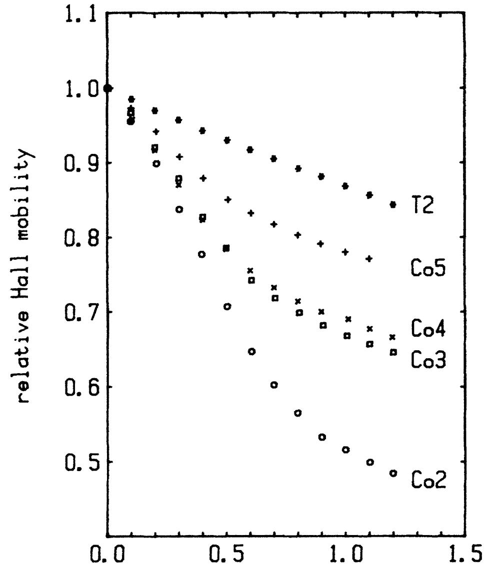

FIG. 4. The pressure variations of relative Hall mobility measured at $T=77$ K.

served variations of both Hall coefficient and Hall mobility (the latter because of the more efficient ionized impurity scattering for the Co^{1+} double acceptor than for the Co^{2+} single acceptor). At sufficiently high pressures (p) the $R_H(p)$ dependence saturates which means that all of the Co^{2+}/Co^{1+} levels are occupied. Thus, the total observed change of the free-electron concentration (Δn) directly corresponds to the initial ($p=0$) concentration of Co ions in the Co^{2+} charge state. Therefore, for each sample the value of Δn should be proportional to the absorption coefficient (α) measured for the ZPL of the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ intra-$3d^7$-subshell of Co^{2+} ions. Table I shows an excellent correlation between Δn and α which could be hardly understood if the observed $R_H(p)$ and $R_H\sigma(p)$ variations did not originate from the $Co^{2+}+e^-_{CB} \rightarrow Co^{1+}$ charge transfer.

III. DISCUSSION

Four key parameters were analyzed. The Co^{2+}/Co^{1+} level energy (E_i) for both 77 and 300 K along with its pressure coefficient, the Co-atom concentration (N_{Co}) and the additional acceptor concentration (N_a) were fitted to obtain the best agreement between the calculated and measured pressure dependencies of the Hall coefficient (R_H) and Hall mobility ($R_H\sigma$). We took into account that both the Γ and L minima of the conduction band can contribute to R_H and σ by using

$$R_H = e\frac{r_\Gamma n_\Gamma \mu_\Gamma^2 + r_L n_L \mu_L^2}{\sigma^2}$$

$$= e(n_\Gamma \mu_\Gamma + n_L \mu_L) , \qquad (2)$$

where r_Γ and r_L are scattering factors, n_Γ and n_L are free-electron concentrations, and μ_Γ and μ_L are the drift mobilities of the Γ and L minima, respectively. We assumed that r_L and μ_L were pressure independent, putting $r_L=1$ and taking from the literature[16] $\mu_L=0.3\mu_{\Gamma_0}$, where μ_{Γ_0} is a drift mobility for the Γ minimum under ambient pressure. The L minimum free-electron concentration (n_L) described within Boltzmann statistics,[16] changed upon pressure due to the pressure dependence of the L minimum position and the pressure shift of the Fermi level. It appeared that at 77 K, the contribution of the L minimum to the transport properties of our samples was very small but at 300 K it could not be neglected. All the band-structure parameters of the nonparabolic Γ minimum as well as the pressure dependence of the effective mass were taken from the paper by Blakemore.[16] The drift mobility (μ_Γ) and Hall scattering factor (r_Γ) were calculated using the following expressions:[17]

$$\mu_\Gamma = \frac{\langle \mu(k)\rangle}{\langle 1\rangle} \text{ and } r_\Gamma = \frac{\langle \mu^2(k)\rangle\langle 1\rangle}{\langle \mu(k)\rangle^2} , \tag{3}$$

where, in general,

$$\langle A\rangle = \int_0^\infty -\frac{\partial f_0}{\partial E} A k^3(E) dE , \tag{4}$$

and f_0 is the distribution function and $k(E)$ is the wave vector.

In the calculations of μ_Γ and r_Γ, we considered ionized impurity (Ref. 18), optical-(Refs. 19 and 20), and acoustic-(Refs. 18 and 21) phonon scattering mechanisms. In our samples, both at 77 and 300 K, ionized impurity scattering was dominant. We took into account four types of ionized scattering centers: double Co acceptors (Co^{1+}), single Co acceptors (Co^{2+}) (the total concentration of both Co acceptors being N_{Co}), shallow, constantly ionized donors (the main dopant of the bulk n-type GaAs used for the preparation of our Co-doped samples), and additional single acceptors which were created during annealing of the samples.

In the calculations of the $R_H(p)$ and $R_H\sigma(p)$ dependences, we accounted for the changes of n_Γ and n_L (as the Co^{2+}/Co^{1+} level traps some free electrons) as well as the changes of μ_Γ and r_Γ (induced by the pressure shift of the Fermi level and the changes of the number of the Co^{1+} and Co^{2+} ionized scattering centers). We used the neutrality equation in the following form:

$$\begin{aligned} n_\Gamma + n_L &= N_d - N_a - N_{Co^{2+}} - 2N_{Co^{1+}} \\ &= N_d - N_a - N_{Co} - N_{Co^{1+}} , \end{aligned} \tag{5}$$

where N_d,N_a, and N_{Co} are the concentration of donors, the concentration of additional (other than Co) acceptors, and the total concentration of Co atoms which are either in the Co^{1+} or Co^{2+} charge state ($N_{Co^{1+}} + N_{Co^{2+}} = N_{Co}$).

The concentration of cobalt atoms in the Co^{1+} charge state is described by the expression

$$N_{Co^{1+}} = \int G(E) \frac{dE}{1 + g \exp\left[\dfrac{E - E_F}{k_0 T}\right]} , \tag{6}$$

where E_F is the Fermi energy, g is a degeneracy factor, and $G(E)$ is the Co^{2+}/Co^{1+} level density of states. In the case of transition $Co^{2+}(d^7) \rightarrow Co^{1+}(d^8)$, $g = g(Co^{2+})/g(Co^{1+})$. The degeneracy factor $g(Co^{2+}) = g(^4A_2) = 4$,[10] but $g(Co^{1+})$ is not known. However, Co^{1+} and Ni^{2+} charge states have the same electronic configuration, $3d^8$, and therefore should have the same structure of levels. The ground state $^3T_1$ of the $Ni^{2+}(d^8)$ configuration is split into three triplets.[22] We assumed that all triplets were so close in energy that at 300 and 77 K they were equally populated giving $g(Co^{1+}) = g(^3T_1) = 9$. For the density of states of the Co^{2+}/Co^{1+} level we adopted either δ-like, $G(E) = N_{Co}\delta(E - E_i)$ or broadened, Gaussian-like,

$$G(E) = N_{Co} \frac{1}{\sqrt{2\pi}\Delta} \exp\left[-\frac{(E - E_i)^2}{2\Delta^2}\right]$$

functions, where Δ is a broadening parameter and E_i stands for the Co^{2+}/Co^{1+} level energy, which under pressure should change according to

$$E_i = E_0 + \left[\frac{\partial E_i}{\partial p}\right] p . \tag{7}$$

The values of N_{Co}, E_0, $(\partial E_i/\partial p)$, and N_a were treated as fitting parameters. For the donor concentration N_d we always took the value of 4.5×10^{18} cm^{-3}, assuming that the compensation of the bulk n-type GaAs used for the preparation of our Co-doped samples was sufficiently small to treat its free-electron concentration as the donor concentration. The broadening parameter (Δ) was not fitted, but for the sake of comparison we made the calculations for a few values of ranging from 5 to 20 meV. For the given values of the fitting parameters we could solve Eq. (6) to find the Fermi energy. This enabled us to find all the concentrations of Eq. (5) and then to perform the mobility calculations to find μ_Γ and r_Γ needed to compute R_H and $R_H\sigma$.

The results of the fitting of our calculations to the experimental data are shown in Figs. 1, 2, and 5. One can see that all the theoretical curves reproduce the experimental points well. The steplike character of the curves is evidently due to the existence of the Co^{2+}/Co^{1+} level. It is clear from Fig. 2 that we obtained better agreement between the calculations and the experimental data if we as-

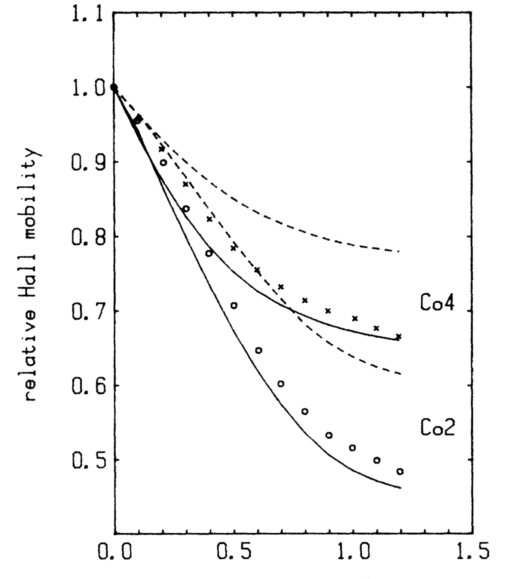

FIG. 5. The Hall mobility versus pressure at $T = 77$ K. Solid lines were calculated for the Co centers undergoing the pressure-induced $-1 \rightarrow -2$ charge transfer, dashed lines for the Co centers replaced by single acceptors ($0 \rightarrow -1$ charge transfer). The density of states of the corresponding level was always assumed to be a Gaussian-like one.

sume the Gaussian-like Co^{2+}/Co^{1+} level density of states (solid lines) rather than δ-like case (dotted lines). In Fig. 5, beside the solid curves corresponding to pressure-induced charge transfer of cobalt ions from -1 to -2 (double acceptor level), we also present dashed lines calculated under the assumption that the level in question corresponds to a single acceptor ($0 \rightarrow -1$ charge transfer). In the latter case the agreement is much worse. This fact provides additional evidence that we really observe the transition to the $Co^{1+}(3d^8)$ double ionized acceptor state.

The Co^{2+}/Co^{1+} level position and its pressure coefficient obtained from our fits are as follows:

$$(E_0 - E_\Gamma)_{T=77\ \mathrm{K}} = 110 \pm 5\ \mathrm{meV}\ ,$$

$$(E_0 - E_\Gamma)_{T=300\ \mathrm{K}} = 140 \pm 5\ \mathrm{meV}\ ,$$

$$\left[\frac{\partial (E_i - E_\Gamma)}{\partial p} \right]_T = -75 \pm 5\ \mathrm{meV/GPa}\ .$$

Because we do not know the real value of the degeneracy factor g (we take $g = \frac{4}{9}$), there could be an additional error in E_0. The change of g by 3 times gives a change in E_0 of approximately $k_0 T$.

The values of other fitting parameters, i.e., N_{Co} and N_a (as well as the values of Δ for which the fittings were performed) for each of the samples are given in Table I. For all of our Co-doped samples the concentration of Co atoms appeared to lie in the range $(0.5-1) \times 10^{18}$ cm^{-3} which is close to the solubility limit of Co in GaAs.[15] Therefore, an increase in the temperature of the duration of the annealing process results mainly in the increase of the acceptor concentration (N_a) but not the value of N_{Co}. Creation of acceptors has already been observed during the Cr-doped GaAs annealing.[23] We obtained reasonably good agreement between the calculated and measured pressure dependences of Hall mobility without introducing a neutral impurity scattering mechanisms (contrary to Cr-doped samples investigated previously[13]). Moreover, our results almost do not change if we additionally take into account neutral impurities with the concentration on the order of 1×10^{18} cm^{-3}.

Although from our results it is evident that the Co^{1+} density of states is well broadened, our data are too limited for a precise determination of the Δ parameter. We think that the observed broadening is a statistical effect originating from the random distribution of impurities (our samples are highly doped ones) and local electric fields given by them. A similar broadening (with similar Δ values) was observed for Cr-doped GaAs.[24]

IV. CONCLUSIONS

The main conclusion of our work is that the Co^{2+}/Co^{1+} double acceptor level in GaAs is degenerate with the conduction band, being 140 and 110 meV above the bottom of the band at 300 and 77 K, respectively. These results mean that at ambient pressure this level is active only in heavily doped n-type samples with $n \geq 3 \times 10^{18}$ cm^{-3}. In the samples with very high free-electron concentration ($n \gg 3 \times 10^{18}$ cm^{-3}), the Co^{2+}/Co^{1+} acceptor level should be completely occupied and no intra-$3d^7(Co^{2+})$-subshell optical transitions could be observed. In the samples with $n \leq 3 \times 10^{18}$ cm^{-3}, the Co^{1+} charge state can be activated by means of hydrostatic pressure which shifts the Co^{2+}/Co^{1+} level down (with respect to the bottom of the conduction band) at a rate of 75 meV/GPa. In this case, one should observe the pressure-induced decrease of the intensity of the $3d^7(Co^{2+})$ optical transitions. Such an investigation is now in progress.

This work was, to our knowledge, the first observation of the Co^{1+} charge state in GaAs.

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