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Charge transfer $Cr^{2+}(d^4) \rightarrow Cr^{1+}(d^5)$ induced by hydrostatic pressure in chromium-doped GaAs

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Hall-effect measurements have been performed on *n*-type GaAs:Cr crystals under hydrostatic pressure up to 11 kbar at 300 and 77 K. These experiments provide evidence for a trapping process of free electrons and a nonlinear variation of their mobility. The interpretation of the results requires that the Cr^{1+} level is degenerate with the conduction band. This energy level is situated 55 meV at 77 K and 115 meV at 300 K above the bottom of the conduction band. The Cr^{1+} level behaves like a trapping center which then scatters the electrons as a double acceptor state. A quantitative fit of the variation of the mobility requires the assumption of a pairing between chromium atoms and donor impurities.

I. INTRODUCTION

This paper deals with the properties of the different charge states of the chromium impurity in GaAs when this impurity occupies a Ga site. The common denomination for these charge states is $Cr^{3+}(d^3)$, $Cr^{2+}(d^4)$, and $Cr^{1+}(d^5)$; this refers to the ionization of the chromium atom. For solid-state physics, Cr^{3+} is a neutral impurity in a III-V compound lattice, Cr^{2+} is a single acceptor state, and Cr^{1+} a double acceptor state. Although these notations are confusing, we shall use them in this paper.

It has been shown recently[1,2] that in *n*-type GaAs:Cr crystals, the stable chromium impurity charge state is $Cr^{2+}(d^4)$ and its fundamental level lies about 0.74 eV above the valence band. In *n*-type GaAs:Cr samples, the stable electron paramagnetic resonance (EPR) Cr^{2+} signal as well as the characteristic intracenter absorption of the Cr^{2+} state $({}^5T_2 \rightarrow {}^5E)$ was observed up to a free-electron concentration $n = 6 \times 10^{17}$ cm^{-1}. These results were in contradiction with the interpretation of the EPR isotropic line $(g = 1.993)$ in GaAs:Cr crystals as being due to the $Cr^{1+}(d^5)$ charge state[3,4] and consequently with the assumption that the second acceptor level Cr^{1+} was lying between the conduction band and the Cr^{2+} acceptor level.[5,6]

However, Kaufmann and Schneider[7] and Stauss *et al.*[8] have recently shown that this EPR isotropic line should be attributed to the $Cr^{4+}(d^2)$ charge state. Furthermore, in a very detailed electrical characterization of various GaAs:Cr samples a second acceptor level of Cr in GaAs was not observed.[9]

In a previous paper,[10] the following has been shown. (i) The intensity of the characteristic Cr^{2+} intracenter absorption decreases significantly under hydrostatic pressure at 77 K for samples with a number of free electrons (n) comparable to that of the chromium impurities (N_{Cr}). (ii) The resistivity of such samples decreases nonlinearly as a function of hydrostatic pressure at 77 K. (iii) If $n < N_{Cr}$ the resistivity increases continuously, whereas the absorption intensity saturates at about 9 kbar. (iv) If $n > N_{Cr}$ the resistivity saturates at about 9 kbar, whereas the absorption strength decreases to zero. These features were interpreted as the pressure-induced trapping of free electrons by the Cr^{2+} centers, which were then converted into a double acceptor state Cr^{1+}. The energy level position of Cr^{1+} was estimated about 70 meV above the conduction-band minimum at 77 K. It was not possible to give a more precise value of this energy because the observed resistivity depends on the free-electron concentration and also on its mobility. Both these values are pressure dependent—the concentration due to a trapping process and the mobility due to a change of the Coulomb scattering and the energy gap. A more detailed analysis of these effects required Hall-effect measurements under pressure, which we have carried out in this study.

This paper presents results of these measurements, the calculation of Cr^{1+} level position as a function of pressure at 300 and 77 K, and also the pressure dependence of the mobility calculations, which requires the assumption of a pairing between acceptor and donor impurities.

II. EXPERIMENTAL CONDITIONS

The Hall measurements were performed at 300 and 77 K using the Van der Pauw method. The high-pressure cell was made with Be-Cu alloy, and the pressure was applied through the compression of helium gas up to 12 kbar, a procedure which preserves the hydrostaticity of the pressure at the liquid-nitrogen temperature.

The samples of GaAs:Cr were obtained by diffusion of Cr into *n*-type GaAs ($n = 10^{18}$ cm^{-3}) as previously described.[2] In these samples an inhomogeneity of the chromium impurity distribution was observed. Thus, it was necessary to make a careful selection of these samples to avoid an inhomogeneity influence on the Hall effect. Ten selected samples were measured and the results for three representative samples (Cr 16, Cr 17, and Cr 19) are presented. These three samples represent three different relative concentrations of free electrons and chromium impurities, $n >> N_{Cr}$, $n > N_{Cr}$, and $n < N_{Cr}$. The fourth possibility, $n << N_{Cr}$, was already discussed[10] and corresponds to a situation for which the number of Cr^{2+} centers remains constant as a function of pressure. The conditions of the sample preparation are recorded on Table I. Beside the GaAs:Cr samples, some test samples of *n*-type GaAs, which had the same technological history, were also measured.

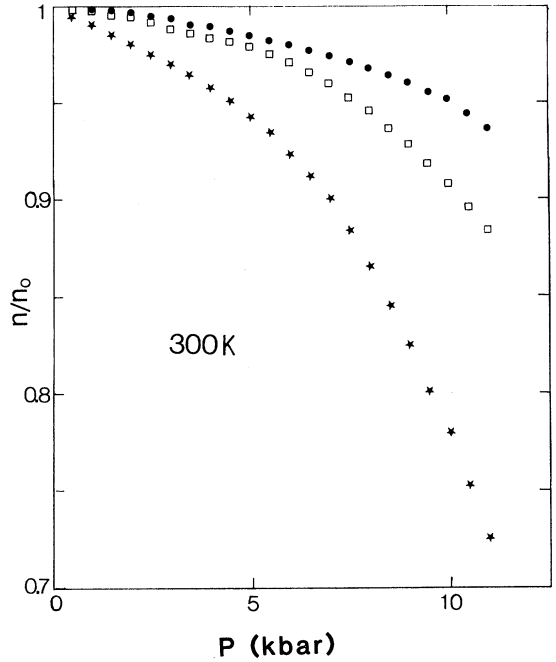

FIG. 1. Relative variation of the free-electron concentration (n/n_0) in *n*-type GaAs:Cr at 300 K under pressure (●—Cr 16, □—Cr 17, ★—Cr 19).

III. RESULTS

The relative pressure dependences of the free-electron concentration and mobility are shown in Figs. 1–4 for 300 and 77 K. The variation of the free-carrier concentration shows that a trapping process occurs at 77 K and ends for the more doped samples near 9 kbar. The mobility curves (Figs. 3 and 4) indicate a new scattering mechanism which we shall discuss later. The pressure ef-

TABLE I. Conditions of preparation and mobility of free electrons for GaAs:Cr samples. n_T and N_{Cr} are the parameters used to fit the $E_i(P)$ curves (Fig. 5) and α the parameter used to fit the mobility variation at 77 K (Fig. 6).

Sample	Diffusion temperature (°C)	Diffusion time (days)	Mobility at 77 K (cm^2/V s)	n_T (10^{18} cm^{-3})	N_{Cr} (10^{18} cm^{-3})	α
Cr 16	1100[a]	1	1500	0.44	0.044	0.5
Cr 17	1100	1	1700	0.36	0.10	0.5
Cr 19	1130	1	1100	0.18	0.21	0.75

[a] Diffused with an extra piece of *n*-GaAs in the same ampoule at a temperature 1120 °C.

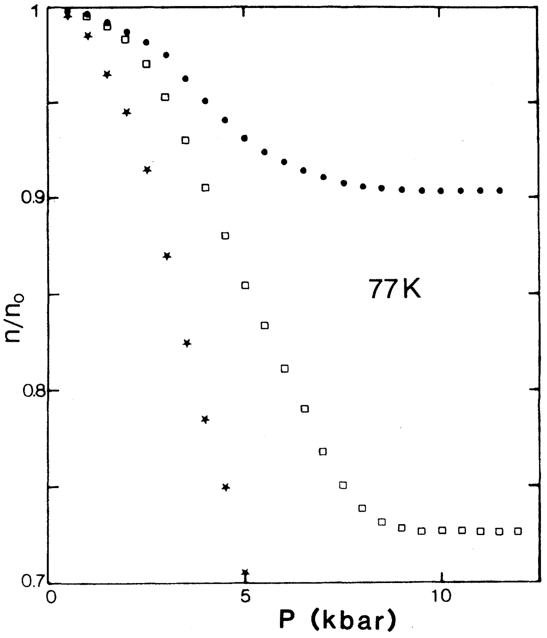

FIG. 2. Relative variation of the free-electron concentration (n/n_0) in n-type GaAs:Cr at 77 K under pressure (●—Cr 16, □—Cr 17,★—Cr 19).

fects were reversible and did not depend on the way a given pressure was reached. In test samples the free-electron concentration was found to be pressure independent at both temperatures.

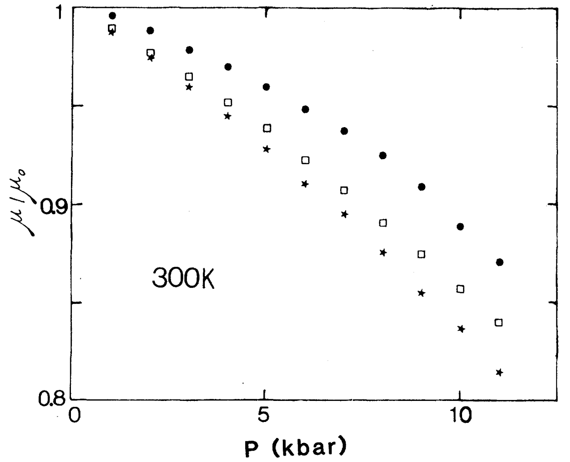

FIG. 3. Relative variation of the free-electron mobility (μ/μ_0) in n-type GaAs:Cr at 300 K under pressure (●—Cr 16, □—Cr 17,★—Cr 19).

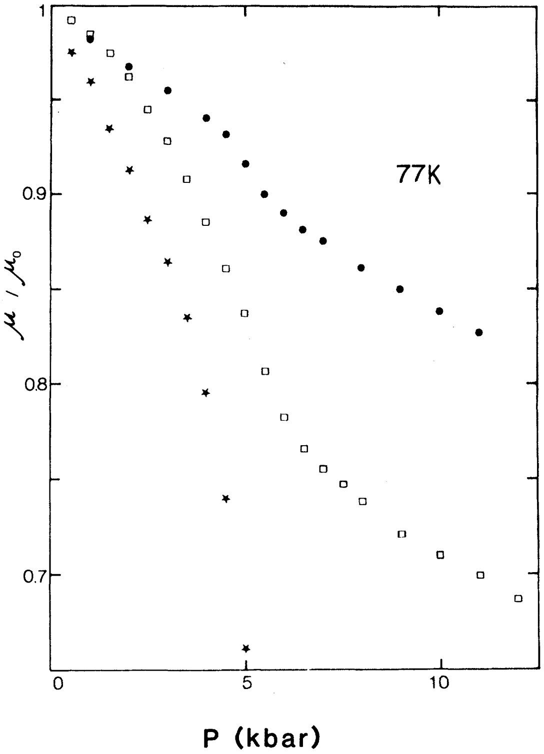

FIG. 4. Relative variation of the free-electron mobility (μ/μ_0) in n-type GaAs:Cr at 77 K under pressure (●—Cr 16, □—Cr 17,★—Cr 19).

A. Discussion

1. Model

The Cr^{1+} charge state in GaAs corresponds to a $3d^5$ electronic configuration and its fundamental state is the singlet level ^6A. This level cannot undergo the Jahn-Teller splitting; also, the spin-orbit splitting should be very weak. This is supported by GaAs:$Fe^{3+}(3d^5)$ and GaAs:$Mn^{2+}(3d^5)$, where the total splitting of $^6A_1$ state is less than 0.1 meV.[11,12] In such a situation it can be assumed that the density of states for the trapping Cr^{1+} centers has a δ-function form. The concentration of free electrons can then be expressed by

$$n = n_T - \frac{N_{Cr}}{1+g\exp\left[\dfrac{E_i - E_F}{kT}\right]}, \tag{1}$$

where N_{Cr} is the concentration of chromium atoms, n_T is the total concentration of free and trapped electrons, E_F and E_i are the Fermi energy and the Cr^{1+} level energy (both measured with respect to the bottom of the conduction band), and g is a degeneracy factor which will be discussed in the next paragraph.

Our samples were analyzed by the secondary-ion mass-spectroscopy (SIMS) technique and have only silicon and tellurium (besides chromium), which are shallow impurities completely ionized at liquid-nitrogen temperature. As already pointed out, the test samples do not show any variation of the free-carrier concentration with pressure. Hence Eq. (1), which assumes that only the chromium impurities can trap the free carriers, is justified.

2. Degeneracy factor

In the case of the transition $\mathrm{Cr}^{2+}(d^4) \rightarrow \mathrm{Cr}^{1+}(d^5)$, according to statistical considerations[13] the electronic degeneracies of both levels must be taken into account. For the $\mathrm{Cr}^{2+}(d^4)$ state, the fundamental level $^5T_2$ is split due to the Jahn-Teller effect into $^5B_2$ and ^5E states, with a separation of 3 times the Jahn-Teller energy, i.e., about 0.25 eV.[10] The ground $^5B_2$ level is also split by the spin-orbit interaction[1] but the separation here is less than 1 meV, and at 300 and 77 K temperatures all these sublevels are populated. Hence for $\mathrm{Cr}^{2+}(d^4)$, only the $^5B_2$ state degeneracy was taken.

In the case of $\mathrm{Cr}^{1+}(d^5)$ the ground-state $^6A_1$ splitting is also smaller than 1 meV (see above), and one obtains, finally,

$$g=\frac{g(\mathrm{Cr}^{2+})}{g(\mathrm{Cr}^{1+})}=\frac{5}{6}\ .$$

The influence of this factor on E_i can be easily calculated. From Eq. (1) one gets

$$E_i=E_F+kT\ln\left[\frac{N_{\mathrm{Cr}}}{n_T-n}-1\right]-kT\ln g\ . \tag{2}$$

The last component is equal to 1.21 meV at 77 K and 4.72 meV at 300 K. It will be shown that this correction is below the experimental uncertainty at least for the liquid-nitrogen temperature results.

3. Calculation of the Cr^{1+} level position

To find the energy of the Cr^{1+} level, we have used expression (2). The value of E_F was calculated for all pressures, since n is known from experiment. The nonparabolicity of the conduction band was taken into account. All the band parameters and nonparabolicity relations were taken from the results of Raymond *et al.*[14] The energy gap pressure coefficient $(\partial E_G/\partial P)$ was taken[15] as 11×10^{-6} eV bar^{-1}.

Finally, E_i is obtained as a function of pressure with two fitting parameters n_T and N_{Cr}. With the assumption that E_i has a linear variation with pressure, the experimental results were fitted to obtain a straight line. The same parameters were used for both temperatures. The results of the fits are presented in Fig. 5. E_i is found to be 55 ± 2 meV at 77 K and 115 ± 2 meV at 300 K, and its pressure coefficient at both temperatures $(\partial E_i/\partial P)_T=(-6.3\pm0.5)\times10^{-6}$ eV bar^{-1} with respect to the bottom of the conduction band. The results obtained for n_T and N_{Cr} are presented in Table I. The values of n_T are very close to those of n at 1 bar deduced from Hall measurements. The values of N_{Cr} can be compared with the intensity of the intracenter Cr^{2+} absorption observed in GaAs:Cr samples.[10] This is in agreement with our previous calibration deduced from the chromium concentration measured by SIMS: The absorption cross section is about 10^{-17} cm^2.

4. Temperature and pressure coefficients of the Cr^{1+} level

The experimental value of the temperature coefficient of the Cr^{1+} level is $(\partial E_i/\partial T)_P$ 2.7×10^{-4} eV/K relative to the conduction band. The temperature coefficient of the energy gap between 77 and 300 K can be estimated[16] as -3.6×10^{-4} eV/K, and hence one can find $(\partial F_i/\partial T)_P=-9\times10^{-5}$ eV/K relative to the valence band. Knowing the temperature and pressure coefficients of the Cr^{1+} level in GaAs, it is possible to evaluate the intrinsic part of the temperature coefficient due to the electron-phonon interaction $(\partial E_i/\partial T)_V$ from the relation

$$\left[\frac{\partial E_i}{\partial T}\right]_P=-\frac{3\alpha}{\chi}\left[\frac{\partial E_i}{\partial P}\right]_T+\left[\frac{\partial E_i}{\partial T}\right]_V ,$$

where α is the linear expansion coefficient[17] and χ is the isothermal compressibility.[18] From the experiments, we obtain $(\partial E_i/\partial P)_T=-6.3\times10^{-6}$ eV bar^{-1} relative to the conduction band. Then assuming $(\partial E_G/\partial T)_P=11\times10^{-6}$ eV bar^{-1} (see above) one obtains $(\partial E_i/\partial P)_T=4.7\times10^{-6}$ eV bar^{-1} relative to the balance band. Taking into

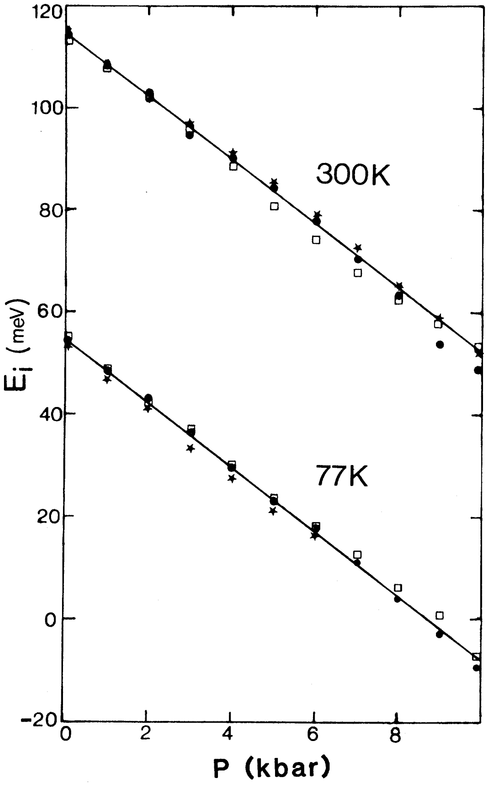

FIG. 5. Variation with pressure of the Cr^{1+} level with respect to the bottom of the conduction band of GaAs at 77 and 300 K (●—Cr 16, □—Cr 17, ✱—Cr 19)

account the fact that the local compressibility for Cr in GaAs was found to be about 20% lower than that of GaAs (Ref. 10) the dilation term can be estimated as about $(-8 \pm 1) \times 10^{-5}$ eV/K. Though this estimation is rather rough, it gives an order of magnitude for $(\partial E_i / \partial T)_V$, which is found to be about 10^{-5} eV/K, so the electron-phonon interaction seems to play a minor role in the variation of the Cr^{1+} level with temperature.

B. Electron mobility under pressure

The mobility of electrons in semiconductors is determined by different scattering mechanisms. These mechanisms are the scattering by neutral impurities (μ_{neutral}), scattering by ionized impurities (μ_{ion}), scattering by acoustic and optical phonons (μ_{ac} and μ_{opt}), and the scattering by free electrons (μ_{el}). All these mechanisms are statistically independent, and the total mobility is given by

$$\frac{1}{\mu} = \frac{1}{\mu_{\text{neutral}}} + \frac{1}{\mu_{\text{ion}}} + \frac{1}{\mu_{\text{ac}}} + \frac{1}{\mu_{\text{opt}}} + \frac{1}{\mu_{\text{el}}} . \tag{3}$$

These different mechanisms can be theoretically evaluated and their relative importance depends on temperature and on the number of carriers.[19] At liquid-nitrogen temperature and for the number of carriers present in our samples, the main contribution to (3) is from the first two mechanisms. The scattering probability due to neutral defects is, in a first approximation, pressure independent, and hence μ_{neutral} varies as the inverse of the effective mass at the Fermi level. The scattering due to ionized impurity depends on pressure in a more complex way. The expression for the mobility due to this mechanism can be written[19]

$$\mu_{\text{ion}} = A \frac{n}{N_i Z_i^2} \frac{1}{m_c^{*2} F_i} , \tag{4}$$

where $A = (3\pi h^3 / 2e^3 m_0^2)\epsilon_0^2$ is proportional to the square of the static dielectric constant, Z_i and N_i are the charge and the concentration of the ionized centers, m_c^* is the effective mass at the Fermi level, and F_i is a function of the screening length λ_i:

$$F_i(\lambda_i) = \ln[1 + (2k_F \lambda_i)^2] - [1 + (2k_F \lambda_i)^{-2}]^{-1} ,$$

where $k_F = (3\pi^2 n)^{1/3}$,

$$\lambda_i = \left[\frac{\pi}{3n} \right]^{1/6} \frac{h}{2e} \left[\frac{Z_i \epsilon_0}{m_c^*} \right]^{1/2} .$$

The last formula is only valid for a strongly degenerate electron gas.

In the calculation we consider two kinds of ionized impurities, the first one due to shallow impurities with a number given by the SIMS analysis, and the second one due to chromium impurities. We assume that the chromium impurities can act as a single (Cr^{2+}) or double acceptor state (Cr^{1+}). It should be noted that a double acceptor state Cr^{1+} (in fact Cr^{2-}) scatters the free carriers about 4 times more efficiently than a single Cr^{2+} (in fact Cr^{1-}) does, as can be seen from Eq. (4). This fact is responsible for the observed nonlinear variation of the mobility as a function of pressure (Figs. 3 and 4). These above contributions to the mobility have been calculated and compared with the experimental results. The calculated curves reproduce the qualitative variation of the mobility but the strength of the calculated scattering process is always too strong. An example of such a result is shown in Fig. 6 for the Cr 17 sample (dashed line).

The possibility of charge compensation in our samples between the donor and acceptor impurities exists. This effect should reduce the scattering efficiency, because the donor and the acceptor centers

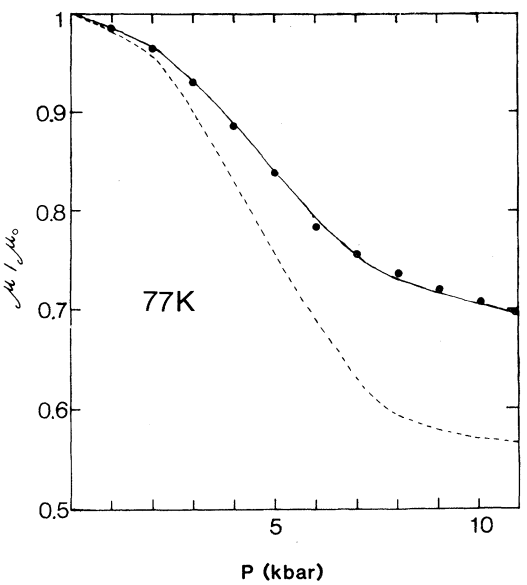

FIG. 6. Experimental points for the Cr 17 sample at 77 K compared with calculated mobility for $\alpha = 1$ (dashed line) and $\alpha = 0.5$ (solid line).

being neighbors will act as dipoles or higher multipoles. A crude approach to this problem is to divide the population of chromium impurities into two classes, (a) one in which the chromium atoms are isolated in the bulk lattice and (b) one in which the chromium atom is paired with a donor impurity. It is worth noting that it may be a first neighbor, also a third, a fifth, etc., up to a distance corresponding to the screening length. For Coulomb scattering such a pair behaves to a first approximation like a neutral impurity when the chromium impurity is in the Cr^{2+} state, or like a single acceptor state when the chromium impurity is in the Cr^{1+} state. If we let α be the proportion of unpaired Cr impurities $(0 < \alpha < 1)$ the mobility can be calculated with α as a fitting parameter. In Fig. 6 a quantitative agreement (solid line) between theory and experiment for the Cr 17 sample is achieved with a value of about 0.5 for α. This value varies with samples of different carrier and impurity concentration but remains always significantly different from 1 (see Table I). This fact $(\alpha < 1)$ can be explained as a statistical effect. The screening length value for the Cr 17 sample is $\lambda_1 \simeq 70$ Å for $Z = 1$, $\lambda_2 \simeq 100$ Å for $Z = 2$. The values lead to a "screening volume" $V_i = \frac{4}{3}\pi\lambda_i^3$ around $10^{-18}\ \mathrm{cm}^3$ and consequently to the conclusion that statistically an important part of the donors should be found inside these "volumes" which surround the chromium impurities.

IV. CONCLUSION

The controversy in the literature about the different charge states of the chromium impurity originated from the previous assignment of an EPR isotropic signal to the Cr^{1+} charge state rather than to the Cr^{4+}. This study shows that the Cr^{1+} charge state is not stable at atmospheric pressure and lifts the last serious difficulty about the assignment of the different chromium-related signals in EPR measurements.

Another difficulty was connected with the interpretation of the well-known 0.84-eV luminescence line. First suggested by White[20] and then confirmed in recent studies,[21–23] this luminescence is probably due to a complex made with a donor-chromium pair, as first neighbors. The proportion of these pairs is probably much less than that we found in our experiments. This is plausible because the luminescence requires a local distortion essentially produced by first-neighbor pairing, whereas the dipole effect involves pairs which can extend much farther. Hence both results are consistent and lead to support the idea that pairing effects between chromium and donor impurities are important in gallium arsenide.

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