Investigation of the absorption of $Cr^{2+}(3d^4)$ in GaAs

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Results on the absorption of intracenter transitions of the Cr^{2+} impurity charge state $(3d^4)$ in GaAs are reported for different samples with various free carrier and chromium concentrations. The analysis of the data gives limiting values for the Jahn-Teller energies in the ground and excited states of the Cr^{2+} impurity. The strengths of these couplings are discussed with different models. The effect of the hydrostatic pressure up to 10 kbars at 300 and 77 K is also reported and it is shown that, in specific conditions, the $Cr^{1+}(3d^5)$ state can be activated by the pressure against the Cr^{2+} state. These experiments prove that the Cr^{1+} energy level is above the GaAs conduction band.

I. INTRODUCTION

In a previous paper[1] (hereafter referred as paper I) the study of the p-type samples doped with chromium has been reported. The n-type samples exhibit an absorption due to chromium impurities in the same range of energies but with a structure and a cross section quite different. Though this absorption has already been the subject of previous publications,[2,3] it has never been explained theoretically with standard models as was done for II-VI compounds, for instance, ZnSe doped with chromium.[4] The absence of interpretation was in part due to the anomalous shape of the absorption itself that no theory was able to reproduce. So a systematic study of this absorption shape in samples with various free-carrier and chromium concentration was undertaken. These samples have been prepared by diffusion of chromium in n-type GaAs doped with silicon and tellurium during the growth, and the details of this preparation have been reported in paper I. We have also given in that paper the results of the different characterization procedures we apply to these samples and especially those of a systematic study of the EPR spectra of each sample. The conclusion was that in most of them, two or three different charge states of the chromium impurity are present at the same time, but that the dominant one for n-type doped samples is Cr^{2+}. The different experimental setup used for the experiments has also been described in paper I and will not be repeated here.

This paper will start by giving directly the results of absorption on n-type samples as a function of the temperature and the way their interpretation can be presented. A detailed discussion about the Jahn-Teller energies and different parameters defining the model is given in Sec. III.

Then results on the absorption of n-type samples as a function of the pressure are given: it is shown that they depend on the relative concentration of free carriers and chromium impurities. For large free carriers doping the charge state, $Cr^{2+}(3d^4)$ is converted to $Cr^{1+}(3d^5)$ at high pressure, the energy level of this latter double acceptor state being degenerated with the conduction band. The last section of the paper is devoted to a discussion which reviews all energy levels which can be associated with the chromium impurity in GaAs.

II. ABSORPTION OF N-TYPE CHROMIUM-DOPED SAMPLES AS A FUNCTION OF TEMPERATURE

A. Experimental results

The EPR spectra of these n-type samples are similar to those already reported in the literature[5] and are characterized by a dominant signal corresponding to the Cr^{2+} charge state. As already pointed out in paper I, these spectra also show a more or less large cyclotron signal which for the highest doped samples limit the possibility of the EPR detection. Nevertheless the Cr^{2+} signal has been detected in all samples. The Cr^{3+} state has an EPR cross section stronger than the Cr^{2+} one, and this signal which is dominant in p-type samples has been seen also in the n-type Cr_7, Cr_6, Cr_5, and Cr_4 samples. All these spectra have been also recorded under the illumination with the IR line of an argon laser (1.09 μm) and the results are that the Cr^{2+} signal never decreases under illumination within the experimental accuracy (~1%). Then it appears that for this state the optical transitions are internal within the levels of the Cr^{2+} impurity. The optical signature of this charge state is made up of a broad band at around 7300 cm⁻¹, which has already been reported[2,6] and which is shown in Fig. 1
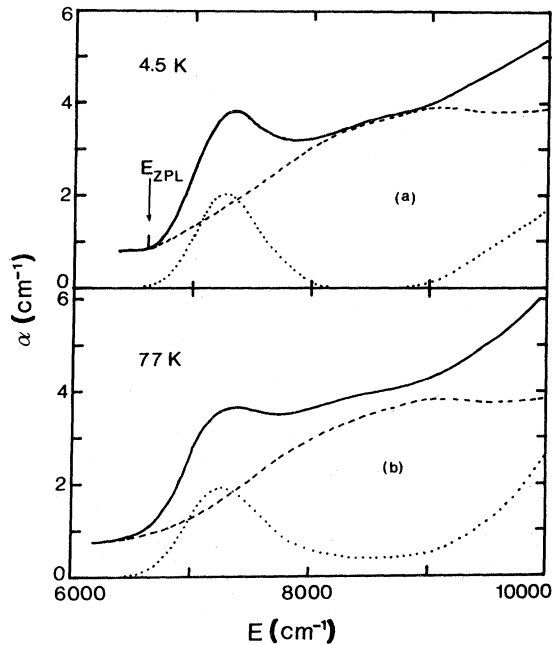
FIG. 1. Absorption spectra (full lines) of the Cr_7 sample at 4.5 K (a) and 77 K (b). The dashed line is the contribution of the photoionization process due to the Cr^{3+} centers and the dotted line is the result of the decomposition of the spectra (see text).

FIG. 2. Configurational diagram (a) and ordering of levels (b) for a Jahn-Teller distorted d^4 configuration in a tetrahedral crystal field coupled to an E mode. The presented ordering of levels corresponds to $V_1 < 0$ and $V_2 > 0$. The allowed transition $^5B_2 \rightarrow {}^5A_1$ is indicated by the vertical arrow.

for the Cr_7 sample. If the assignment of this band has always been accepted, the correlated emission band has been the subject of a large controversy.[7] For chromium-doped samples with a small number of carriers, a luminescence band with a zero-phonon structure at 0.839 eV appears. This zero-phonon structure has at least nine components and has been assigned to the luminescence due to the Cr^{2+} state by many authors. This was in contradiction with the results of EPR measurements and far-infrared spectroscopy at high magnetic field[8] on Cr^{2+} which give for the ground state at $^5B_2$ level in an environment of D_{2d} symmetry [Fig. 2(b)], which leaves only three possible split levels by the spin spin-orbit interaction. In fact, we have shown recently[9] by absorption measurements on the Cr_7 sample that the zero-phonon line has three components and that its energy of 0.82 eV (6619 cm^{-1}) is well below the 0.839-eV line. More recent experiments, performed with a better resolution[10] on samples which are ten times thicker than ours, have shown that this spectrum consists in fact of seven lines, the position and relative intensity of which indicate that the excited state is subject to a dynamical (or even zero) Jahn-Teller effect and not to a static one.

The shape of the absorption band such as the one reported in Fig. 1 has never been explained,
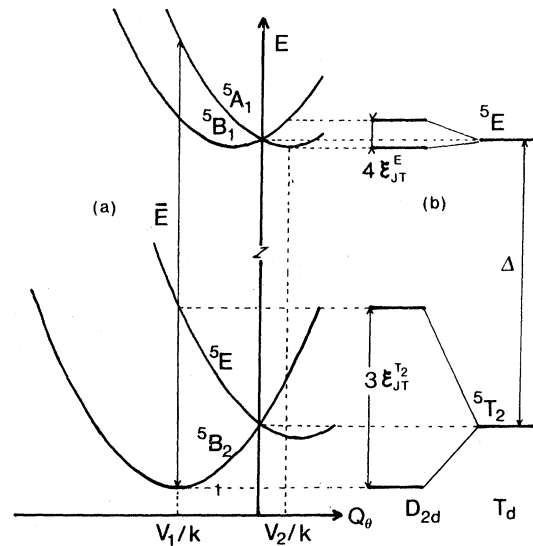
though it is typical of the Cr^{2+} absorption in GaAs, whatever the procedure of doping is.[2] The similar absorption in II-VI compounds[4] as well as in GaP (Ref. 6) always decreases to zero at high energy. In GaAs this absorption never decreases to zero and even sometimes there is no absolute maximum in the spectrum. We know, from a theoretical point of view and whatever is the model, that such an intracenter absorption has a shape which is not far from a Gaussian curve. So it is clear that there is an extra absorption due to chromium impurities which is always present, not always of the same strength with respect to the intracenter absorption, and typical of chromium in GaAs. This absorption cannot involve the Cr^{2+} level as the inital state because from this level the absorption is first-order forbidden towards the conduction band, which is described by s-like wave functions. Such an absorption would lead to a decrease of the Cr^{2+} signal in EPR measurements under illumination, and this is not observed. Furthermore, this extra absorption has never been observed either in II-VI compounds or in GaP.

So there remain two possibilities: either an absorption involving a chromium impurity in a site different from the gallium site, or a photoionization absorption due to a charge transfer between Cr^{3+} and Cr^{2+}. We have rejected the first possibility because we know nothing about these configurations and because it would be surprising that

such an effect would not depend significantly on the method of preparation of the samples. On the other hand, the last possibility is appealing for many reasons: (i) The shape of this photoionization absorption is a very broad band, the study of which has been reported in paper I. It has some light singularity around 8600 cm^{-1} which is found again in the spectra. (ii) We know, at least for our samples, that when the EPR detection is possible, then exist some Cr^{3+} states in n-type samples. (iii) The optical cross section of the photoionization process is much larger than that of the intracenter absorption (see below). So only a small percentage of chromium in the Cr^{3+} state can give rise to comparable absorption coefficients. (iv) The superposition of both absorptions is specific for chromium impurity in GaAs because this is the only compound where both absorptions occur in the same range of energies (within 500 cm^{-1}). (v) If the interpretation is correct, since we know the behavior of the photoionization spectra as a function of temperature and pressure (see paper I), we should find by subtracting, for each sample, a constant percentage of $Cr^{3+} \rightarrow Cr^{2+}$ transitions, a behavior of the intracenter absorption which is reasonable. This was done for all our samples at all temperatures and pressures.

Figure 1 shows the decomposition we have made to extract the intracenter absorption curve from the experimental one. The dashed line is proportional to the photoionization absorption curve (see paper I) and is fitted in intensity at 8700 cm^{-1} and 4.5 K to the experimental curve. It remains a Gaussian-type curve (dotted line) centered at 7280 cm^{-1} and a tail on the high-energy side which can be easily explained as the end-of-the-tail states due to the shallow impurities. As a matter of fact, this tail follows quite well the variation of the gap with temperature and pressure.

B. Interpretation of the results

The lowest free-ion ^5D state of $Cr^{2+}(3d^4)$ is split by the crystal-field potential of T_d symmetry, by an amount defined as the crystal-field splitting Δ, into an excited orbital doublet ^5E and a ground-state orbital triplet $^5T_2$ [Fig. 2(b)]. These levels which are degenerate will suffer a Jahn-Teller effect that lowers the symmetry and induces a tetragonal distortion of D_{2d} symmetry (along $\langle 100 \rangle$ directions) as is revealed by EPR measurements.[5] This distortion reflects the transfer of an electronic to an elastic energy absorbed by the bulk material. The type of distortion observed, as well as the results of EPR measurements under uniaxial stress,[11] show that this transfer is made by phonons of

E symmetry to which electronic levels are strongly coupled, as in the case of II-VI compounds.[12]

Assuming a linear Jahn-Teller coupling and neglecting the spin-orbit interaction, the relevant Hamiltonian consistent with the symmetry requirements is[12]

$$\mathcal{H}_{JT} = V_1(Q_\theta \mathcal{E}_\theta + Q_\epsilon \mathcal{E}_\epsilon) + V_2(Q_\theta \mathcal{U}_\theta + Q_\epsilon \mathcal{U}_\epsilon)$$
$$+ \tfrac{1}{2}k(Q_\theta^2 + Q_\epsilon^2)J, \qquad (1)$$

where V_1 and V_2 are the coupling coefficients of the lattice to the orbital $^5T_2$ and ^5E states, respectively. The Q_θ and Q_ϵ are the dimensionless parameters which measure the magnitude of the lattice distortions. $\mathcal{E}_\theta$ and $\mathcal{E}_\epsilon$ ($\mathcal{U}_\theta$ and $\mathcal{U}_\epsilon$) are electronic operators which operate on the orbital $T_2(E)$ wave functions. The last term of Eq. (1) is the elastic energy, J is the unit matrix, and k is related to the effective mass μ and to the phonon frequency ω by $k = \mu\omega^2$. Following the notation of Ham,[13] V_1 is negative and V_2 positive for the ordering of levels found for II-VI compounds.[4] The different couplings of the $^5T_2$ and ^5E states to E modes is described by Sturge[14] and it is convenient for a graphical illustration to represent only a section of the adiabatic potential-energy surfaces by the $Q_\epsilon = 0$ plane [Fig. 2(a)]. With these notations the Jahn-Teller energies of the $^5T_2$ and ^5E levels are given by

$$\mathcal{E}_{JT}^{T_2} = V_1^2/2k \text{ and } \mathcal{E}_{JT}^E = V_2^2/2k,$$

respectively. It is then easy to show that if $\bar{E}$ measures the energy of the maximum of the absorption band of the $^5B_2 \rightarrow ^5A_1$ transition and E_{ZPL} that of the zero-phonon line, then

$$\bar{E} - E_{ZPL} = \frac{(V_1 - V_2)^2}{2k} = \mathcal{E}_{JT}^{T_2}\left(1 - \frac{V_2}{V_1}\right)^2, \qquad (2)$$

with

$$E_{ZPL} = \Delta + \mathcal{E}_{JT}^{T_2} - \mathcal{E}_{JT}^E.$$

The theory of the line shape of these transitions in the linear coupling approximation[15] gives a fractional intensity of the zero-phonon line with respect to the total absorption band of e^{-S}, where $S = (V_1 - V_2)^2/2k\hbar\omega$ is the Huang-Rhys parameter. Then from (2):

$$\bar{E} - E_{ZPL} = \hbar\omega S, \qquad (3)$$

which says that S is a measure of the mean number of phonons of energy $\hbar\omega$ emitted after the absorption at $\bar{E}$. We obtain from the experimental results:

$$E_{ZPL} = 6619 \text{ cm}^{-1},$$

$$e^{-S} \simeq 3.3 \times 10^{-4}, \text{ and } \bar{E} = 7280 \text{ cm}^{-1}.$$

We then deduce that $S \simeq 8$ and from (3), $\hbar\omega \simeq 82$ cm^{-1}. The experimental value e^{-S} is similar to that found for ZnSe by Vallin *et al.*[16] This value of S corresponds to a case of a relatively strong electron-lattice coupling which justifies the use of the semiclassical model described by Lax[17] to reproduce the line shape $I(E)$ of the absorption band. In this approximation, this line shape is Gaussian:

$$I(E) = \frac{1}{(\pi\Gamma^2)^{1/2}} \exp\left(-\frac{(E-\bar{E})^2}{\Gamma^2}\right), \qquad (4)$$

with Γ^2 given by

$$\Gamma^2 = \frac{(V_1 - V_2)^2}{k} \hbar\omega \coth\frac{\hbar\omega}{2kT}$$

$$= 2(\bar{E} - E_{ZPL})\hbar\omega \coth\frac{\hbar\omega}{2kT}.$$

The expression for Γ^2 has exactly the same structure as that found for the photoionization process [see paper I, Eq. (9)] and can be generalized in the same way to different types of phonons. But it turns out that in this case only one type of phonon is sufficient to reproduce the experiments. We do not expect a significant contribution of a symmetrical relaxation here, since the transitions do not change the number of electrons around the impurity.

The fit of the experimental curve to a Gaussian shows that the departure from it is only noticeable on the high-energy side and well below the maximum. So we can measure Γ^2 on the low-energy side which gives a mean value of Γ for different samples at liquid-helium temperature $\Gamma = 340 \pm 5$ cm^{-1}. It is possible, on the other hand, to calculate Γ since we know S and $\hbar\omega$ independently. This gives $\Gamma = 330$ cm^{-1}, which in view of the various approximation made in the model can be considered a good check.

The value of $\hbar\omega$ found here is naturally assigned to the E phonon inducing the Jahn-Teller distortion. This value corresponds quite well to the transverse acoustic value of the phonons of GaAs along the [100] direction. This result is also found in II-VI compounds.[4] The origin of this phonon is not clear since in a cluster model which is usually the physical picture taken to understand the properties, the TA modes at X correspond to an X_5 irreducible representation (Ga site as origin) which generates, in the group T_d spanned by the different functions of the star of k_X, only T_1 or T_2 modes.[18] In this range of phonon energies the only bulk phonons which could generate E phonons are the TA modes at the K point. In zinc-blende compounds, the density of states for phonons in

this region is very high and the activation of such phonons by the impurity can likely be dominant.

C. Absolute cross section

Knowing the absorption value at 7280 cm^{-1} for the samples Cr$_6$ and Cr$_7$ and their chromium concentration measured by secondary ion mass spectroscopy (SIMS) (see paper I), it is possible to give the absorption cross section of the intracenter transition. One finds $\sigma(Cr^{2+}) \simeq 1 \pm 0.2 \times 10^{-17}$ cm^2. The correlative maximum cross section of the photoionization process (Cr$^{3+}\rightarrow$ Cr^{2+}) was found on the order of 10^{-16} cm^2 (see paper I). It was then clear that even with a small number of Cr^{3+} centers in the n-type samples, this latter absorption is still important.

III. DISCUSSION ABOUT THE JAHN-TELLER ENERGIES

We now try to estimate the Jahn-Teller energies for this system. Krebs and Stauss[11] have recently reported uniaxial stress measurements on the EPR Cr^{2+} signal in GaAs. From these measurements and using a cluster model for their interpretation, they proposed the following set of values to describe the Jahn-Teller effect on the $^5T_2$ level:

$$V_1 = -0.85 \text{ eV/Å},$$

$$\mathcal{E}_{JT}^{T_2} > 1500 \text{ cm}^{-1}, \text{ and } \Delta \simeq 5500 \text{ cm}^{-1}.$$

We want to show that these values for V_1 and $\mathcal{E}_{JT}^{T_2}$ are nonconsistent and probably nonrealistic. They would correspond to a positive value of V_2/V_1 [Eq. (2)] which means that V_2 should also be negative. There are two different models to interpret the Jahn-Teller effect and we shall see that within these two models, the deduced parameters are quite different from those proposed by these authors.

A. Point-charge model

Within this cluster model the different parameters are given by[19]

$$\Delta = \frac{27}{20} \frac{|eq_L|}{4\pi\epsilon_0 R} \frac{\langle r^4 \rangle}{R^4}, \qquad (5)$$

$$V_1 = -\tfrac{4}{7} \sqrt{2} \frac{\Delta}{R} (\tfrac{27}{20}\beta + 1), \qquad (6)$$

$$V_2 = \tfrac{3}{7} \sqrt{2} \frac{\Delta}{R} (\tfrac{9}{5}\beta - 1), \qquad (7)$$

where ϵ_0 is the dielectric constant of the vacuum, R the chromium-ligand distance, q_L the effective charge on the ligand ion, $\beta = \langle r^2 \rangle R^2 / \langle r^4 \rangle$, and $\langle r^n \rangle$

is the average of r^n taken over the radial part of the $3d$ wave function of Cr^{2+}. These last parameters which are known for the isolated ion are found to vary significantly when the ion is merged into a host lattice, due to the spreading of the d-orbitals. So, in prinicple, V_2 could be negative from Eq. (7), whereas V_1 is always negative.

The value of $\delta_{JT}^{T_2}$ obtained by Krebs and Stauss implies $V_2 < 0$ and then $\beta < \frac{5}{9}$. Introducing this value into Eq. (6) leads to $|V_1| < \sqrt{2}\, \Delta/R$. The upper limit for Δ is the energy $E_{ZPL} \simeq 6620$ cm^{-1}. Using $R = 2.44$ Å for GaAs, one gets $|V_1| < 0.48$ eV/Å, a value which is inconsistent with that proposed by Krebs and Stauss. The origin of this strong discrepancy is probably due to the presence of random strains in the sample measured by these authors, strains which are always present and can be dominant in the range of pressure below 200 bars. This difficulty was already pointed out by Vallin and Watkins[12] in the analysis of the same kind of measurements on II-VI compounds. It is likely that it is also at the origin of the same discrepancy found with piezoacoustical measurements.[20] In fact, Cr^{2+} in GaAs should have similar properties with Cr^{2+} in ZnSe,[4] because the distance R is practically the same for both compounds and the effective charges on the As and Se ligands should not be very different. We then believe that in this case too, V_2 should be positive, leading to $\beta > \frac{5}{9}$ and $|V_1| > \sqrt{2}\, \Delta/R$. Now, if $V_2 > 0$, from Eq. (2), $\delta_{JT}^{T_2} < 660$ cm^{-1} and at the same time:

$$\bar{E} = \Delta + 2\delta_{JT}^{T_2} - \frac{2V_1 V_2}{2k} < \Delta + 2\delta_{JT}^{T_2}, \quad \text{since now } V_1 V_2 < 0.$$

Therefore, $\bar{E} - 2\delta_{JT}^{T_2} < \Delta < E_{ZPL}$, the lower limit being still minimized by introducing the upper limit 660 cm^{-1} of $\delta_{JT}^{T_2}$. We then get

$$5960 \text{ cm}^{-1} < \Delta < 6620 \text{ cm}^{-1}.$$

Then $|V_1|$ should be larger than $\sqrt{2} \times 5960/R$ $= 3450$ cm^{-1}/Å $= 0.43$ eV/Å. Using the relation $\delta_{JT}^{T_2} = V_1^2/2k$ (Sec. II B) with $\hbar\omega = 82$ cm^{-1}, we get

$$\delta_{JT}^{T_2} \geqslant 360 \text{ cm}^{-1}.$$

So we end with the following limits:

$$360 \text{ cm}^{-1} < \delta_{JT}^{T_2} < 660 \text{ cm}^{-1},$$

$$0 < -V_2/V_1 < 0.35, \tag{8}$$

$$0 < \delta_{JT}^{E}/\delta_{JT}^{T_2} < 0.12,$$

results which are not very far from those found for ZnSe.[4] The question arises as to whether these results are dependent on the cluster model since this model is rather devoted to the case of ionic compounds.

B. Angular overlap model

This model is believed to be more appropriate to the case of covalent compounds, and we shall try to estimate the Jahn-Teller coupling constants in the framework of it. Bacci[21] has derived the equivalent relations to (5), (6), and (7) in this model. Using the values of the matrix elements

$$\langle \xi | \frac{\partial V}{\partial S_\xi} | \xi \rangle = \frac{2\sqrt{6}}{3R} (e_\sigma - \tfrac{1}{3}e_\pi) \quad \text{for the } {}^5T_2 \text{ level}$$

and

$$\langle \theta | \frac{\partial V}{\partial S_\theta} | \theta \rangle = -\frac{4\sqrt{2}}{3R} e_\pi \quad \text{for the } {}^5E \text{ level,}$$

one gets

$$\Delta = \tfrac{4}{3}(e_\sigma - \tfrac{4}{3}e_\pi), \tag{9}$$

$$V_1 = -\frac{4\sqrt{2}}{3R}(e_\sigma - \tfrac{1}{3}e_\pi), \tag{10}$$

$$V_2 = \frac{4\sqrt{2}}{3R}e_\pi, \tag{11}$$

where e_σ and e_π are the energy changes of the $3d$-metal orbital due to the interaction with the σ or π ligand orbitals. Here e_σ is always positive because it is interpreted as due to the d-orbitals becoming σ antibonding by combination with ligand σ orbitals. e_σ is much greater than e_π and then V_1 is always negative. But e_π (and then V_2) can be positive or negative depending on whether the d orbitals are becoming π antibonding or π bonding by combination with filled or empty ligand orbitals.

In the molecular-orbital scheme, the ordering of complex orbitals should be that of a $(CrAs_4)^{4+}$ complex ion, and following the corresponding diagram[22] in which the coupling to the t_1 ligand π orbitals is neglected, we find that the combination of d orbitals to the ligands ones are π antibonding. So e_π and then V_2 are found positive within this scheme.

Combining Eqs. (9), (10), and (11), we get V_1 $= - (\sqrt{2}\, \Delta/R) + V_2$ and then here too, $|V_1| > \sqrt{2}\, \Delta/R$. So the set of parameters given in (8) is still valid in this scheme. This last discussion is based on the antibonding character of the orbitals of the electron trap Cr^{2+}. This result is in accordance with a recent theory developed for substitutional deep traps in covalent semiconductors[23] which shows that this property is general.

C. Experimental investigation

A direct measure of the Jahn-Teller energy for the fundamental ${}^5T_2$ level should be given by the optical transition between the ${}^5B_2$ and ${}^5E$ levels which are optically split by $3\delta_{JT}^{T_2}$ (Fig. 2). In the II-VI compounds,[4] this transition gives rise to a

A. M. HENNEL *et al*.

weak and broad absorption band in the infrared, so we have tried to measure it on the sample Cr_7. Unfortunately, we are confronted by two main difficulties: (i) the Cr^{2+} charge state is dominant only when the samples are still n-type and then in the range of absorption coefficients we are looking for, the dominant mechanism of absorption is still that of the residual free carriers. (ii) Due to the relatively low limit of solubility of Cr in GaAs, our samples have a chromium concentration one order of magnitude less than the II-VI compounds samples for which such an absorption is in the range of 1–2 cm^{-1}.

We have nevertheless performed the experiment in the infrared down to 77 K. The absorption coefficient after subtraction of a constant background (~ 0.6 cm^{-1}) is plotted as a function of $(1/\omega)^2$, which allows to show the free-carrier absorption known to vary like λ^2. A straight line is then fitted to this plot and any deviation of it is supposed to be due to an extraabsorption. In the range of energies between 900 cm^{-1} and 5000 cm^{-1}, no significant absorption higher than 0.2 cm^{-1} has been detected, so we do not have any experimental information which directly measures the Jahn-Teller energy. However, we think after the recent absorption measurements[10] that the more plausible value for the Jahn-Teller energy should be very close to the upper limit given by (8).

IV. RESULTS ON THE ABSORPTION OF N-TYPE CHROMIUM-DOPED SAMPLES AS A FUNCTION OF PRESSURE

When the absorption of the n-type samples is measured under pressure, we observe three types of behavior depending on the relative concentration of free-carrier n and chromium impurities N_{Cr}.

A. Samples with $n \ll N_{Cr}$

This is the case for samples Cr_6 and Cr_7. In this situation, we observe what we could call a "normal" behavior. The absorption strength is practically independent of pressure and the spectrum varies gently as is shown in Fig. 3 for the Cr_6 sample. The decomposition of these curves has been made for different pressures with the procedure described in Sec. IIA, using a given proportion of photoionization transitions which have been sealed to the measured variation under pressure of such transitions (see paper I). We then get a set of Gaussian-type curves for which the energies of the maximum vary under pressure as reported in Fig. 4. Within our experimental error, the width of these curves does not vary with pressure, which means that, in a first approximation, the Jahn-Teller energy does not vary with pressure. This is coherent with the result reported in paper I. Assuming this point, the observed variation of $\bar{E}$ with pressure (Fig. 3) is then given by that of Δ. Therefore, $d\bar{E}/dP$ $\simeq d\Delta/dP = -5\Delta d\ln R/dP$ in the framework of the point-charge model.

We have plotted in Fig. 3, as a dashed line, the expected variation of Δ:

$$d\Delta/dP = (5K/3)\Delta,$$

using for K the known compressibility of GaAs. This quantity varies at a rate of 2×10^{-6} eV/bar, whereas the experimental value is 1.6×10^{-6} eV/bar.
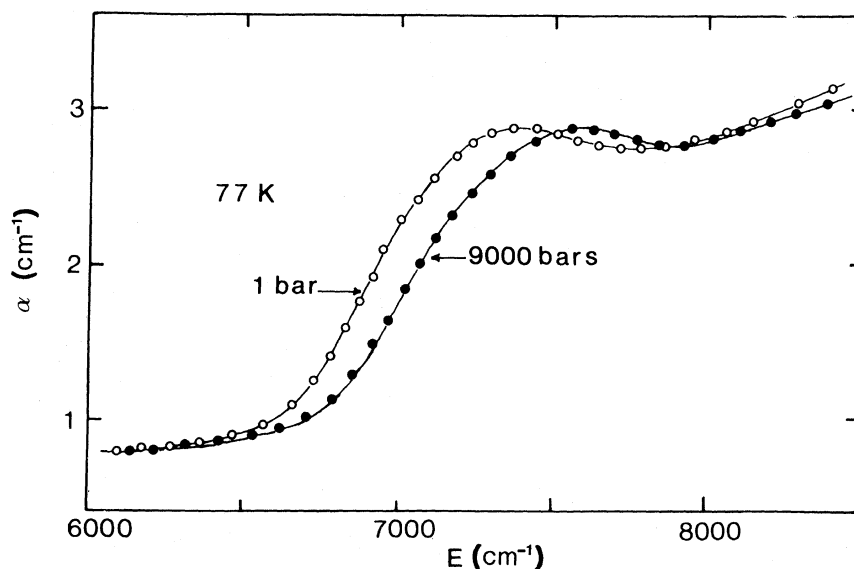

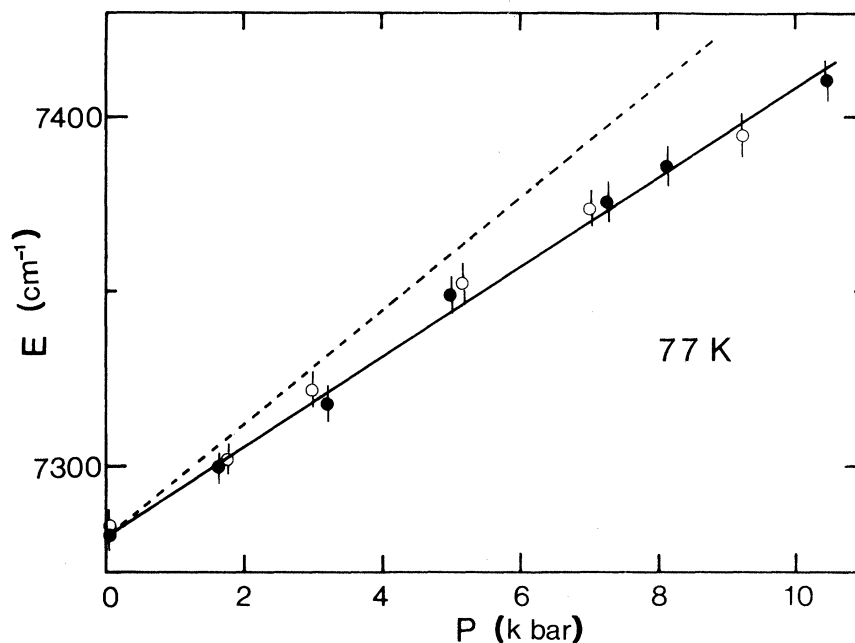FIG. 3. Absorption spectra of Cr_6 sample at 77 K and as a function of the pressure.

FIG. 4. Variation of the energy $\bar{E}$ of the intracenter absorption at 77 K (full dots) and 300 K (empty dots) as a function of pressure. The dashed line is representative of the theory with the bulk compressibility.

The same type of discrepancies were obtained by Stephens and Drickamer[24] on ZnS doped with nickel and cobalt. To reduce this discrepancy, one is led to assume that the local compressibility of the medium is significantly different from that of the host lattice. We then find here a local compressibility about 20% lower than that of GaAs. This value which may seem large, is in fact not very surprising. Zigone et al.[25] by model calculations have tried to calculate the local modes of the transition-metal impurities in ZnS crystals, and reached the conclusion that the force constants should be increased by 50% in order to reproduce the experimental results. This gives a decrease of local compressibility by an amount of 30 to 40%, which is larger than our result but could be explained by the fact that this model neglects the relaxation of the ligands and then overestimates the force-constant defect.

So, the sign as well as the magnitude of the change of the local compressibility are plausible. In order to compare the pressure coefficients of transitions involving the levels of deep impurities with those of bulk transitions, we are then led to correct the experimental values for this change. For instance, the transition from the valence band to the $^5T_2$ level varies experimentally at a rate of 3×10^{-6} eV/bar (see paper I). Then if the valence-band deformation potential is known, the renormalized deformation potential of the $^5T_2$ level is obtained from the experimental one by increasing

it in the ratio of the bulk-to-local compressibilities.

The fact that the absorption strength does not vary significantly with pressure can be considered as a support to the model of linear coupling for the transitions. When this is not the case, Curie et al.[26] have shown that this absolute strength should vary significantly under pressure due to the different distortions of the fundamental and excited vibronic levels.

B. Samples with $n \leqslant N_{Cr}$

This is, for instance, the case of samples Cr_4 and Cr_5. For them, the behavior under pressure is quite different. The spectra of Cr_4 are shown in Fig. 5. The strength of the intracenter absorption decreases and at the same time a very broad absorption extending over more than 3000 cm^{-1} increases with pressure. During the same experimental run, the resistivity of the sample has been measured and increases very sharply as is reported in Fig. 6, together with the decreasing variation of the cross section of the intracenter absorption. These two experimental facts can be interpreted as follows: The intracenter absorption is the optical "signature" of the Cr^{2+} charge state. Its decrease means that this charge state progressively disappears under pressure. The abrupt change in the resistivity has to be, at least in part, connected to the trapping of free carriers in the sample by some deep acceptor level. So gath-
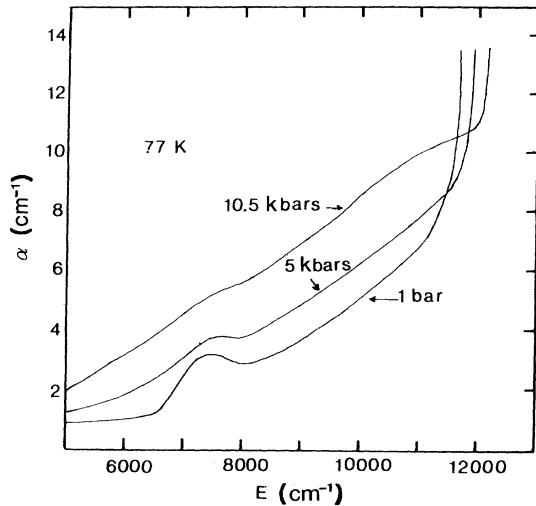
FIG. 5. Variation of the absorption spectra of the Cr$_4$ sample with pressure and at 77 K.

ering these two facts leads to the conclusion that, under pressure, the Cr^{2+} level (in fact a one-electron trap) is progressively converted into a Cr^{1+} level (a two-electron trap). This transfer is possible when the Fermi level for free carriers overlaps the Cr^{1+} level, an overlap induced by pressure which increases the gap at a rate of 11×10^{-6} eV/bar compared to that for the impurity level $\sim 3 \times 10^{-6}$ eV/bar. So, at 1 bar and 77 K, the Cr^{1+} level should lie well inside the conduction band.

These effects are, of course, reproducible but also reversible and do not depend on the way a given pressure is reached, i.e., by increasing or decreasing it. The fact that it remains some residual Cr^{2+} charge state means that at high pressure all electrons are practically trapped,
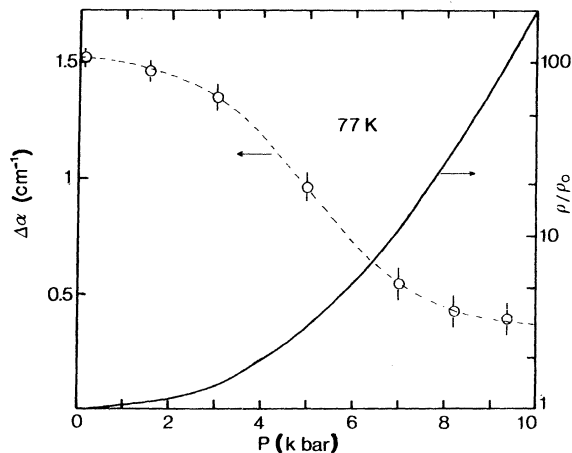
and since $n < N_{Cr}$, some Cr^{2+} centers are not converted into Cr^{1+}. On the other hand, the broad absorption band which appears should be assigned to transitions involving the Cr^{1+} level. The optical transition between the fundamental level of Cr^{1+} ($^6A_1$) and the conduction band is possible by a photoionization process which takes advantage of the mixing of s and p functions of the conduction band due to the nonparabolicity. This process involves first-order forbidden electronic transitions, but the interpretation of it which could be done in principle by a similar formalism to that developed in paper I, would require the knowledge of such spectra for different temperatures.

C. Samples with $n > N_{Cr}$

This is the case for samples Cr$_1$ and Cr$_2$. The situation here follows logically from the preceding one. The intracenter absorption decreases and then disappears while the broad absorption increases. The resistivity of the sample first increases and saturates as is reported in Fig. 7. The interpretation is straightforward with our model, since, when $N_{Cr} < n$, all chromium centers can be converted into Cr^{1+} and then some free carriers remain, giving the residual conductivity.

We could try, using a simple model and neglecting a change in the mobility, to locate the Cr^{1+} level inside the conduction band. This would probably be questionable because a careful inspection of the experimental data under pressure shows that the change in the resistivity is significantly larger than a simple trapping process would predict. So the mobility variation is also probably nonlinear and significant, as would be expected from our model since the Coulomb scattering by a two-electron trap is roughly four times higher
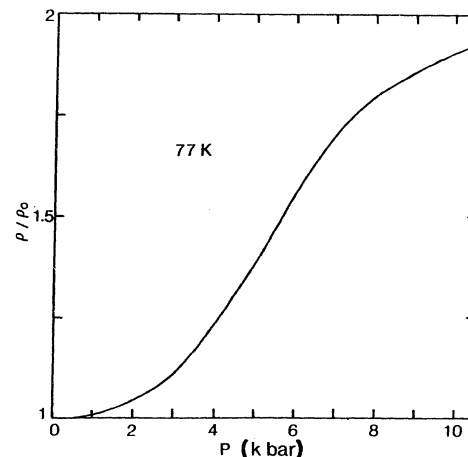

FIG. 6. Variation as a function of pressure of the intracenter maximum absorption ($\Delta\alpha$) and of the relative resistivity (ρ/ρ_0) for the Cr$_4$ sample at 77 K.

FIG. 7. Variation of the relative resistivity of the Cr$_1$ sample as a function of pressure at 77 K.

than that of a one-electron trap. We can however, tentatively give for the Cr^{1+} level an energy of 60 ± 20 meV above the conduction band at 77 K and 1 bar.

A more precise value and a detailed analysis of the effects involved by such a trapping require Hall-effect measurements under pressure, which were not possible with the optical high-pressure cell but which are now in progress using another apparatus.

V. ENERGY LEVELS OF CHROMIUM IMPURITY IN GaAs

We have now the possibility to locate most of the energy levels given by the chromium impurity in GaAs. From the results of paper I, the thermal energy E_T of the fundamental $^5B_2$ level of Cr^{2+} lies above the valence band at 0.735 eV, whereas the optical threshold E_0 for this level is 0.915 eV. With the present results, the thermal energy of the $^5A_1$ excited level of Cr^{2+} lies 0.820 eV (6619 cm^{-1}) above E_T and then 1.555 eV above the valence band. So this level is degenerated with the conduction band at 77 K by about 35 meV. This explains the existence of impurity-induced photoconductivity and photo-Hall effects as was reported by Look.[27] The optical energy which referred to the maximum of the intracenter absorption is about 0.90 eV. The thermal energy of the fundamental $^6A_1$ Cr^{1+} level is also degenerated with the conduction band by about 60 ± 20 meV at 77 K and then lies above that of the $^5A_1$ excited level of Cr^{2+}.

CONCLUSION

This report on the absorption spectra due to the intracenter absorption of Cr^{2+} in the n-type gallium arsenide has shown that the impurity behaves quite the same way as that in zinc selenide. The ground state of the impurity suffers a "static" Jahn-Teller effect probably larger than that of ZnSe, whereas the excited level would, rather, exhibit a dynamical effect. In both cases, the distortion is found to correspond to a contraction of the tetrahedron. The analysis of the different energy levels with respect to the band levels confirms that the excited level is degenerated with the conduction band. The cross section of the absorption has been obtained from comparison with the impurity analysis and appears to be stronger than that of II-VI compounds.

The study of the pressure effect on these transitions has revealed that the local compressibility should be significantly lower than the bulk one. For a free-carrier concentration comparable to that of the chromium, the observed effect has been analyzed as a pressure-induced activation of the Cr^{1+} level which appears to be degenerated with the conduction band. A more detailed evaluation of the parameters and properties of this level requires measurements of the Hall effect under pressure, measurements which are now in progress.

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