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Interpretation of luminescence in GaAs: Cr: 0.839 eV and 0.574 eV lines

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Résumé. — La raie de luminescence à 0,839 eV dans GaAs dopé chrome est généralement interprétée comme étant une transition interne à Cr²⁺ (5E-5T₂) en site substitutionnel. Cette interprétation n’est pas en accord avec les résultats de R.P.E. et d’absorption en infra-rouge lointain.

White a proposé une interprétation en termes de recombinaison excitonique sur un centre iso-électronique. Nous proposons ici une autre explication où la raie à 0,839 eV résulte de la transition interne d’un ion 5D (d⁴ ou d⁶) en symétrie C₃V. La raie à 0,839 eV correspond à la transition 5E*-5E*. L’état excité 5E* est correctement décrit par une théorie de champ cristallin statique tandis que l’état fondamental 5E nécessite une description vibronique E ⊗ ε en symétrie trigonale. Pour cet état, nous obtenons un rapport Eₗ/ℏω = 2.2. Les niveaux de structure fine à 1,50 meV et 2,56 meV sont interprétés comme les deux premiers niveaux vibroniques excités (A₁, A₂) dont la dégénérescence (accidentelle pour un couplage linéaire) a été levée par un léger effet non linéaire. La structure fine de l’état fondamental E est décrite à l’aide d’un opérateur Lᵦ ayant subi un facteur de réduction p = 0.03. Des considérations à un électron permettent d’interpréter la raie à 0,839 eV comme étant due à un ion Cr²⁺ (d⁴) en site gallium couplé à un donneur de la colonne VI en site substitutionnel, ou à un ion Cr⁰ (d⁶) en site interstitiel couplé à un accepteur en site arsenic.

La raie de luminescence à 0,574 eV est interprétée comme étant due à la capture d’un trou sur le même centre.

Abstract. — The 0.839 eV luminescence line in GaAs: Cr is generally interpreted as an internal transition in Cr²⁺ ion (²E-³T₂) on gallium site. This interpretation does not agree with E.P.R. and far-infrared absorption results.

White has proposed an interpretation as an excitonic recombination on an isoelectronic deep centre. We propose an alternative explanation in which the 0.839 eV line would be an internal transition in a 5D ion (d⁴ or d⁶) in C₃V symmetry. The 0.839 eV line would correspond to a ²E*-³E transition and the 0.75 eV hump to the ³E*-³A₁ transition. The excited state ²E* is satisfactorily described by a crystal field treatment whereas the ³E ground state needs a vibronic description E ⊗ ε in trigonal symmetry. For that state we get a ratio Eₗ/ℏω = 2.2. The fine structure levels I and J respectively at 1.50 and 2.56 meV are interpreted as the first two excited vibronic states (A₁ and A₂) by including a weak non linear coupling. The fine structure of the ground state ³E is described using an operator Lᵦ submitted to a reduction factor p = 0.03. One electron considerations lead to the interpretation of the 0.839 eV line as a transition related either to a Cr²⁺ ion (d⁴) on gallium site coupled to a donor (sixth column) on arsenic site or to a Cr⁰ ion (d⁶) interstitial coupled to an acceptor on arsenic site.

Moreover, the luminescence line at 0.574 eV is interpreted as the transition corresponding to the capture of a hole on the same centre.

Introduction. — The technological importance of semi-insulating gallium arsenide (field effect transistors, logical circuits) as well as the difficulties encountered in its use both as epitaxial substrate and as implantation substrate have led to a lot of studies related to that material. Optical spectroscopic measurements (photo and cathodoluminescence [1-9], absorption [10-14], D.L.O.S. [15]), magnetic studies [16-23] as well as electrical measurements (D.L.T.S. [24-26], O.C.T.S. [27-29]) have been used coupled sometimes to chemical analyses (Spark Source Mass Spectroscopy, Atomic Absorption... [30-31]). A great
variety of other methods have also been used; for example transport properties: Hall effect [32-33], alternative conductivity [34], photoconductivity and photoHall [35-44], TSC...

All the measurements carried out on a large variety of samples (bulk: Bridgmann or Czochralski, epitaxial: VPE or LPE), having or not been subjected to some technological preparations, (annealing, implantation, diffusion...) have still not led to an overall view of the properties of chromium in gallium arsenide.

In this paper, we shall deal with the luminescence properties of chromium doped GaAs and show that, if chromium is often an isolated impurity on gallium site, other sites or complexes must be introduced to explain some of the data.

In part I, we are going to review the main published results. Then, in part II, some new results concerning the 0.81 eV band and the 0.535 eV line are shown. In part III, we try to interpret the 0.839 eV transition starting from symmetry considerations that lead us to explain the high degeneracy of the 0.839 eV line and the origin of the 0.75 eV hump by an internal transition of a chromium ion (Cr$^{2+}$ or Cr$^0$) complexed with a first neighbour (C$_{3v}$ symmetry). Then, in 3.2, a static description of the system is given leading to a good quantitative agreement for the excited state. In 3.3, a vibronic description is made in which the ground state features are quantitatively explained. In part IV, we propose to interpret the 0.574 and 0.535 eV lines by relating them to the same complex centre. Finally, the main consequences of our model are drawn in part V.

1. Published results. — In this paragraph, we shall point out what are, in our opinion, the properties of GaAs: Cr that are well understood. For that, we shall review the main published results.

1.1 Electron Spin Resonance. — E.S.R. measurements performed by Krebs and Stauss [17-21], Kaufmann and Schneider [16] have shown that chromium could exist, at least, under three charge states: Cr$^{3+}$, Cr$^{2+}$ and Cr$^+$. Up to now, the first two charge states have only been found to be stable and they define a level in the band gap corresponding to the isolated chromium on Ga site (single acceptor; neutral = Cr$^{3+}$ or ionized = Cr$^{2+}$). Cr$^+$ is obtained under optical excitation and is interpreted as an evidence for the existence of a doubly ionized charge state of chromium isolated on gallium site. If that was the case, and if that state was in the band gap, one should find a stable Cr$^+$ signal and no Cr$^{2+}$ signal in materials where the Fermi level is close enough to the conduction band. That was not observed by Clerjaud et al. [45] who detected stable Cr$^{2+}$ in n-type Cr-diffused samples. Furthermore they interpret hydrostatic pressure measurements [46] by placing the Cr$^+$ level above the conduction band minimum. Hence, following E.S.R., the second acceptor level of chromium isolated on gallium site is not in the gap. As a consequence, the double acceptor Cr$^+$ should only be excited with light on energy larger than 1.5 eV and thus the isotropic signal at $g = 1.993$ observed by Kaufmann and Schneider cannot be Cr$^+$ on gallium site.

1.2 Luminescence and Absorption. — A lot of luminescence bands are found in GaAs: Cr (0.57, 0.574, 0.61, 0.64, 0.68, 0.81, 1 eV) and thus their interpretation is difficult. The main results are: the 0.57 and 0.61 eV bands are related to chromium on gallium site and interpreted respectively as [47]:

\[
\text{Cr}^{2+} + \text{hole in the valence band} \rightarrow \text{Cr}^{3+} + h\nu = 0.57 \text{ eV}
\]
\[
\text{Cr}^{3+} + \text{electron in the conduction band} \rightarrow \text{Cr}^{2+} + h\nu = 0.61 \text{ eV}
\]

The 0.81 eV band shows a zero-phonon line (ZPL) at 0.839 eV. That line has received several interpretations. Up to now, the most commonly accepted was an internal transition $^3E - ^3T_2$ in Cr$^{2+}$ [2, 5, 6, 8]. Some authors have shown that this interpretation could not stand [47, 48, 49]. The main reasons are:

— The ground state splitting of the 0.839 eV line, as resolved by Lightowlers et al. [5, 6] does not fit with the splitting that is deduced from the E.S.R. measurements [18] and confirmed by far-infrared absorption [12]: E.S.R. shows a four levels ground state whereas the optical measurements at 0.839 eV are interpreted by a six levels ground state.

— Another absorption band at 0.92 eV with a ZPL at 0.820 eV has been resolved by Clerjaud et al. [45], and has been interpreted as the internal transition $^5B_2 (^5T_2)$-$^5A_1 (^3E)$ in Cr$^{2+}$. The ground state $^1B_2 (^5T_2)$ agrees with E.S.R. measurements on Cr$^{2+}$ in GaAs, and with the results obtained on other materials: GaP [50] and II-VI compounds [51, 52].

Therefore, another interpretation must be found for the 0.839 eV line and the 0.81 eV associated band.

The 0.64 eV (and 0.68 eV) bands are related to the incorporation of Ga$_2$O$_3$ in the melt [47, 53, 54, 55]. The 1 eV band has still no reliable interpretation and finally the origin of the 0.574 eV band is not obvious.

In absorption, a transition has been related to the photoionization Cr$^{3+}$ + electron in the valence band → Cr$^{2+}$ [14]. As said above, a band at 0.9 eV [10] with its zero-phonon line at 0.820 eV [45] corresponds to the internal transition in the Cr$^{2+}$ ion.

The 0.9 eV absorption band is observed in n-type Cr-doped samples, as well as the 0.61 eV band is in luminescence. Thus for optical measurements as for
E.S.R. measurements, Cr$^{2+}$ is the stable state in n-type samples and isolated chromium on gallium site acts as single acceptor. Neither absorption nor luminescence have been related to Cr$^{3+}$ internal transition.

1.3 Electrical Measurements: D.L.T.S., O.C.T.S., Hall Effect... — D.L.T.S. experiments have been performed on chromium doped GaAs [24-26]. They have led to the observation of a unique trap (HL1) and the thermal parameters of this centre have been deduced very precisely around 350 K [25]. The extrapolation at 0 K of the values is less accurate and is not in contradiction with the values given by Hennel et al. [14] from absorption measurements. The correlation between these two experiments is being performed by D.L.O.S. [56] and the first results seem to show that they are both dealing with the same level. The conclusion would thus be again that chromium isolated on Ga site is a single acceptor.

Transport experiments, which have been carried out by several authors [32, 33, 44] can only be interpreted by using a preexisting model. For some authors chromium is a single acceptor, for others, it is a double acceptor. The transport results show that, in some samples, two deep acceptors are present in the gap. A good fit is obtained by assuming that chromium is a double acceptor, but transport experiments alone cannot show that this is truly the case. Other measurements [29] have shown that a lot of levels are present in the band gap of GaAs : Cr.

1.4 Summary. — It is obvious that isolated chromium substitutional to gallium gives only rise to a single acceptor level near the centre of the gap (the double acceptor level being degenerated with the conduction band [46]). Almost all the associated transitions have been found: Cr$^{3+}$ + electron in the valence band $\rightarrow$ Cr$^{2+}$ : 0.92 eV by absorption [14], 0.57 eV in luminescence [47] and 0.7 eV for thermal activation energy at 350 K (D.L.T.S. [25]).

Cr$^{2+}$ $\rightarrow$ Cr$^{3+}$ + electron in the conduction band : 0.61 eV in luminescence [47] and 0.7 eV for thermal activation energy at 350 K [25]. The absorption transition has not been detected.

The internal transition in Cr$^{2+}$ ($^5\!B_2$-$^3\!A_4$) has been observed at 0.820 eV in absorption [45]. The associated luminescence has not been detected yet [57].

These results are summarized on the figure 1 in terms of two configurational coordinate diagrams: one at 0 K and the other at 350 K.

The spectroscopic properties of substitutional chromium are almost understood, and it is accepted that this acceptor level, together with the EL$_2$ deep donor and, in some cases, together with other deep acceptors is the main responsible for compensation in GaAs : Cr [58]. On the contrary, some properties of GaAs : Cr are not understood yet:

— origin of the 0.839 eV and 0.574 eV luminescence lines.
— explanation of the fast diffusion properties: it is now accepted that chromium diffuses from the substrate into the epitaxial layer [59]. It is also known that chromium redistributes during annealing [60, 61] but the mechanisms are not understood [62],

— origin of the isotropic E.S.R. signal at $g = 1.993$, so called « Cr$^+$ »,
— role of silicon and of oxygen doping during growth...

This paper is an attempt to explain the luminescence properties, but we will show that consequences can be derived concerning the other unexplained properties.

2. Experimental results. — We have analysed the luminescence of a large number of chromium doped GaAs samples. The experimental setup has already

**Fig. 1.** — Configurational coordinate diagram for chromium substitutional on gallium site (Cr$^{3+}$-Cr$^{2+}$) at 0 K and 350 K. The 0 K diagram is from Deveaud et al. [51] and the 350 K diagram is from Martin et al. [25]. $^3\!A_4$ and $^3\!B_2$ states are defined in [51].
been described [7]. The detection is made with a PbS cell at 200 K, the excitation with a 4 W argon laser and the sample temperature can be set between 4 and 300 K. Most of the samples came from RTC but we have studied samples from other suppliers (all of them were Bridgman grown) and also chromium diffused samples [47]. This work has led us to the following conclusions.

The 0.839 eV line intensity is related to the chromium concentration in the sample [7]. For equivalent chromium concentrations, it appears that silicon incorporation, in the melt, low enough for the sample to remain semi-insulating, increases its intensity whereas Ga2O3 addition seems to have no influence [54]. Our experimental resolution does not allow us to confirm the results of Lightowlers et al. [5, 6] : only four components are resolved in the spectrum at 4 K. But we have noticed, as all authors have, that the band presents a hump at 0.75 eV. This hump appears in all spectra with the same shape and thus the two bands belong to the same transition and it cannot be simply attributed to a 2LO phonon replica [63] : we have tried a classical fit following Huang-Rhys [64] and the figure 2 shows that we cannot obtain a good fit. In order to fit the spectrum a gaussian band, centred at 0.76 eV, must be added.

A temperature study of the 0.839 eV band clearly shows (Fig. 3) that the band is in fact composed of two distinct components. If the whole band would correspond to a phonon replica, as usual, the temperature dependence of the half width would be:

\[ W = W_0 \left( \coth \frac{\hbar \omega}{2 kT} \right)^{1/2} \]

where \( \hbar \omega \) is the energy of the involved phonon. By fitting our results with such a law, we get (see Fig. 4) a phonon energy of 7.5 meV which is not compatible with the experiment : the dominant phonon has an energy of 9 meV. We have thus been led to fit all the curves of figure 3 with two gaussians centred respectively around 0.76 eV and 0.82 eV. As the figure 3 shows, we obtain good results between 60 K and 260 K. The temperature dependence of the half width that we obtain gives then a phonon energy of 9 meV for the 0.82 eV band (as expected) and of 8.5 meV for the 0.76 eV band (see Fig. 5).

As a conclusion, the 0.81 eV band is composed of two bands always associated, the first one has a zero phonon line and phonon replica whereas the second one is centred near 0.76 eV at 4 K and does not show any zero-phonon line. That was to be expected because the mean number of emitted phonons, deduced from the width at 0 K (68 meV) and from the phonon energy (8.5 meV), is too large.
Fig. 4. — Temperature dependence of the half width of the whole 0.839 eV band. This dependence gives a phonon energy of about 7.0 meV which is not in agreement with the energy of 9.0 meV corresponding to the phonon replica.

\[ W = W_0 \left( \coth \frac{\hbar \omega}{2 kT} \right)^{1/2} \]

\[ W_0 = 88.2 \text{ meV} \]

\[ \hbar \omega = 7 \text{ and } 7.5 \text{ meV} \]

Fig. 5. — Temperature dependence of the half width of the two gaussian bands fitting the 0.839 eV band (see Fig. 4). The lower curve correspond to the band centred at 0.82 eV and the upper one to the band centred at 0.76 eV. The involved phonon energies are respectively 9 meV and 8.5 meV.

The 0.574 eV line can appear with [2, 53] or without [5] the broad 0.57 eV band. The 0.574 eV line is never seen under YAG laser excitation. We think that this 0.574 eV line is related to chromium and not to another transition metal ion because the luminescence of Fe [3], Mn [65], V [66], is already known and because Co and Ni doped samples that we have studied [67] do not present that luminescence line. So the line seems not to be due to an impurity introduced together with chromium but is due to chromium itself. The luminescence spectrum of a high [Cr] and high [Si] sample, near 0.574 eV and near 0.535 eV is presented on figure 6. The 0.535 eV line has already been interpreted as a local mode phonon replica of the 0.574 eV band [68]. The spectrum of figure 6 shows that the two lines have comparable shapes but their intensity ratio (~ 1/10) remains constant when the temperature ranges between 10 K and 40 K. This is not compatible with the statement that the 0.535 eV line is a phonon replica of the 0.574 eV line.

Fig. 6. — Photoluminescence spectrum of the high [Cr] and [Si] sample near 0.55 eV. The lower curve is the zero-phonon line near 0.574 eV (lower scale) and the upper curve is the replica near 0.535 eV (upper scale).

3. Interpretation of the 0.839 eV line. — This luminescence line is clearly related to the presence of chromium in the sample and because of its sharpness, is an internal transition. Its main characteristic is a
very high degeneracy; optical measurements [5, 6, 69] are consistent with six levels in the ground state and five levels in the excited state. We have checked that such a high degeneracy was not an isotropic effect.

3.1 SYMMETRY CONSIDERATIONS. — In order to obtain a model that would be able to give a sufficient number of levels for the ground state (six at least), both a two or three-fold orbital degeneracy and a high spin are needed.

In $T_d$ symmetry (undistorted site), the only cases giving enough levels in the fine structure are $d^4$ ($Cr^{2+}$) and $d^6$ ($Cr^0$). The $Cr^{2+}$ absorption having been identified at 0.820 eV the only possible remaining case would be $Cr^0$ (interstitial chromium). But such a model would not take into account the 0.75 eV hump and so it will not be considered here.

The $C_{3v}$ symmetry is the first one that comes to mind after the $T_d$ symmetry. It is very easy to obtain the $C_{3v}$ symmetry: by coupling the chromium atom to an impurity or to a defect on the first neighbour site. The chromium atom can be either interstitial or substitutional: In $C_{3v}$ symmetry, $d^4$ or $d^6$ ions alone are likely to give a high number of levels in the fine structure. $d^4$ would be chromium substitutional on gallium site ($Cr^{2+}$) and $d^6$ an interstitial chromium ($Cr^0$). Both $d^4$ and $d^6$ free ions have as ground state term ($Hund's$ rules): $^3D$ ($L = 2, S = 2$). The $C_{3v}$ crystal field lifts the degeneracy of the free ions and gives: $D'$ (free) $\rightarrow$ $\Gamma_1 + 2 \Gamma_2$ ($= \Gamma_1 + 2 E$ following Mulliken's notation). Coupling between orbital states and the $S = 2$ spin gives fine structure levels whose representations are:

For the orbital state $\Gamma_1(A_1)$ : $\Gamma_1 + 2 \Gamma_2$

For the orbital state $\Gamma_5(E)$ : $2 \Gamma_1 + 2 \Gamma_2 + 3 \Gamma_3$.

If the trigonal field $C_{3v}$ is assumed to be only a perturbation of the cubic field, we get the diagram shown on the figure 7. If the $A_1$ state is between the two $E$ states, such a $C_{3v}$ symmetry gives a sufficient degeneracy for the ground state and the excited state of the 0.839 eV line. Furthermore, if the splitted $^3E$ ($^3T_2$) state is the lowest the 0.75 eV hump can be explained by the $^3E^*$ (upper) to $^3A_1$ transition (see Fig. 7). The order of levels that could explain, in both cases $d^4$ and $d^6$, the 0.839 eV line properties is from the lowest state to upper state, $^3E$ (from $^3T_2$), $^3A_1$ (from $^3T_2$) and $^3E^*$.

To get the order of the orbital levels ($^3E$, $^3A_1$, $^3E^*$) that represent $N$-electrons states, they may be formed by starting from one electron states in $C_{3v}$ symmetry (Slater determinants formation and then configuration interaction). The order of the one electron levels will determine, by the excitations of the one electron configuration, the order of the $N$-electrons levels.

$d^4$ : $Cr^{2+}$ on gallium site (Fig. 8a).

In this case, two surroundings are possible, one with arsenic atoms as first neighbours and the other with gallium atoms. When a $d^6$ substitutional ion is submitted to a $T_d$ crystal field, the $t_2$ orbitals feel a negative potential due to the electronic density of the $t_2$ bonds (from hybridization $sp^3$ of both ion and ligands). The

$d^6$ : $Cr^0$ on interstitial site (Fig. 8b).

In that case, the $e$ and $t_2$ orbitals are permuted for the reasons given in the text.

![Diagram](attachment:image_url)
The $t_2$ level is thus above the $e$ level. When the d$^6$ ion is interstitial, there is no $sp^3$ hybridization and the $t_2$ orbitals, that have some bonding character, can undergo a chemical bond (a correct description should be an sd$^2$ hybridization). If so, the $t_2$ levels are below the $e$ levels and the situations is inverted compared to the classical situation for a d$^6$ substitutional ion. Such an explanation has already been used to explain E.S.R. results on interstitial transition metal ions in silicon [70].

With such an assumption, the right order of levels can be obtained for $a_1$ above $e$ (from $t_2$). The potential necessary to get such a situation is a negative potential that destabilizes the d$^2$ orbital (belonging to $a_1$). This potential can be created by an ionized acceptor of the fourth column (Si, C) or a negatively charged arsenic vacancy if the chromium is in an arsenic surrounding...

A complex chromium-impurity (C$_{4v}$ symmetry) can thus explain qualitatively the structure of the 0.839 eV band if chromium has 4 or 6 electrons in the d shell. We shall now expose quantitative calculations.

3.2 STATIC CRYSTAL FIELD THEORY. — The ion embedded in the crystal is represented by an Hamiltonian $H$:

$$ H = H_0 + H_C + H_T + \lambda LS $$

where $H_0$ is the free ion Hamiltonian without spin-orbit coupling, $H_C$ and $H_T$ are the cubic and trigonal potential respectively, $\lambda LS$ is the spin-orbit coupling.

We assume that the perturbation $H_C + H_T + \lambda LS$ only acts within the sub-space $^5D$, whose degeneracy is $(2L + 1)(2S + 1) = 25$. As a basis of the $^5D$ subspace, we take:

$$ |u^+> = \frac{1}{\sqrt{3}} |+2> + \frac{\sqrt{5}}{\sqrt{3}}|-1> $$ basis for $E^*$

$$ |u^-> = \frac{1}{\sqrt{3}} |-2> - \frac{\sqrt{2}}{\sqrt{3}}|1> $$

$$ |x_0> = |0> $$ basis for $A_1$

$$ |x^-> = \frac{\sqrt{2}}{\sqrt{3}} |+2> - \frac{1}{\sqrt{3}}|-1> $$ basis for $E$

$$ |x^+> = \frac{\sqrt{2}}{\sqrt{3}} |-2> + \frac{1}{\sqrt{3}}|1> $$

where $\{|2>, |1>, |0>, |-1>, |-2>\}$ are the spherical harmonics for $L = 2$.

The crystal field operators $H_C$ and $H_T$ can be expressed, using the irreducible tensorial operators $T^{\pm}_{\pm 3}$, by:

$$ H_C = 2\sqrt{70} \left\{ T^4_0 + \frac{10}{7} (T^2_3 - T^4_3) \right\} Dq $$

$$ H_T = \sqrt{70} \left\{ T^2_3 \right\} D\sigma + \frac{10}{7} T^4_0 - \frac{10}{7} (T^2_3 - T^4_3) \right\} D\tau. $$

The matrix elements are calculated using the Wigner-Eckart theorem:

$$ \langle LM_L | T^k_0 | LM'_L \rangle = (-1)^{1-\mu_L} \left( \begin{array}{cc} L & k \\ -M_L & M_L' \end{array} \right) \langle L \parallel T^k \parallel L \rangle $$

$$ \left( \begin{array}{cc} L & k \\ -M_L & M_L' \end{array} \right) \rangle $$

where $\langle L \parallel T^k \parallel L \rangle$ are a 3 j symbol and a reduced matrix element respectively given by the table of Rotenberg et al. [67] and by the table of Nielsen et al. [72]. The parameter $M$ represents the magnitude of the mixing of $E$ and $E^*$ states by the trigonal field of the hamiltonian $H_C + H_T$ are (expressed in the old basis):

$$ \frac{\sqrt{1-M^2}}{1-M^2} |u^+> + M |x^+> $$

$$ \frac{\sqrt{1-M^2}}{1-M^2} |u^-> + M |x^-> $$

$$ |x_0> $$

$$ -M |u^+> + \frac{\sqrt{1-M^2}}{1-M^2} |x^+> $$

$$ -M |u^-> + \frac{\sqrt{1-M^2}}{1-M^2} |x^-> $$

For a given $Dq$ (cubic field parameter), the trigonal field can be characterized by two independent parameters ($D\sigma$ and $D\tau$ or $W$ and $M$). $M$ has already been defined and $W$ represents the magnitude of the $^5T_2$ splitting (see Fig. 7).

Taking for the cubic field parameter:

$$ 10Dq = 6 \text{ 800 cm}^{-1} $$

for the trigonal field parameter $W$ the value deduced experimentally as being the difference 0.84-0.75 eV, i.e. 700 cm$^{-1}$, and $\lambda = -50 \text{ cm}^{-1}$ (d$^6$ ion), we get

$$ 2\sqrt{70} \left\{ T^4_0 + \frac{10}{7} (T^2_3 - T^4_3) \right\} Dq \text{ (2)} $$

$$ \frac{10}{7} T^4_0 - \frac{10}{7} (T^2_3 - T^4_3) \right\} D\tau \text{ (3)} $$

$$ \text{Fig. 9. — Energy levels of the excited } ^5\text{E}^* \text{ state as a function of the mixing parameter } M \text{ (see text). A good agreement with experiment is found for } M = -0.03. $$

for the $^5E^*$ state a fine structure spectrum that depends on the mixing parameter $M$ (see Fig. 9). A good agreement is obtained with the experimental overall
splitting for $M = -0.03$. In that case, there are six levels. This static description gives for the $^3\text{E}^*$ level a splitting close to the structure given by Voillot et al. [69].

For the ground state, the influence of the trigonal field magnitude on the fine structure is shown on figure 10. Whatever the value $W$, the overall splitting we get (about 250 cm$^{-1}$) does not correspond to the experimental result (18 cm$^{-1}$) because the spin-orbit coupling lifts the degeneracy at the first order. Such a discrepancy enforces the use of a reduction factor. It is known that a vibronic description of the system allows to introduce important reduction factors in some cases [73, 74]. Such a vibronic description seems consistent because no static distortion has been introduced in our group theory calculations. This implicitly introduces a dynamic Jahn-Teller effect.

![Fig. 10. - Fine structure of the $^5\text{A}_1$ and $^3\text{E}$ states as a function of the trigonal field strength $W$ (static crystal field description). The spin-orbit coupling lifts the degeneracy at the first order of perturbation and thus the overall splitting of the $^3\text{E}$ state is too large.](image)

3.3 Vibronic Description of the Ground State $^5\text{E}$. — In order to deal with the vibronic coupling, it is necessary to order the energies corresponding to the different perturbations $E_{\text{JT}}$ (Jahn-Teller energy), $W$ (trigonal field), $\lambda$ (spin-orbit constant) The situation where $E_{\text{JT}} \gg W$ and $\lambda$ has been formally solved by Ham [74]. He has shown that, in such a case, the matrix elements of a purely non diagonal operator acting in a vibronic sub-space (generated by a $T_2 \otimes \varepsilon$ coupling and having for basis $\{ \Psi_{\varepsilon}, \Psi_{\varepsilon^*}, \Psi_{\varepsilon^*} \}$), are readily obtained by starting from the off diagonal elements of the same perturbation acting on the corresponding electronic sub-space, and by multiplying them by a unique reduction factor. In a first order perturbation theory the reduction factor is $\gamma = \exp -3 E_{\text{JT}}/2 \hbar \omega$ where $\hbar \omega$ is the energy of the involved phonon. The spin-orbit coupling being purely off diagonal, taking in our case a reduction factor $\gamma = 0.03$ (determined by the overall splitting of the 0.839 eV ground state), and for $\hbar \omega$ the energy deduced from the phonon replica ($\hbar \omega = 9$ meV) a Jahn-Teller energy $E_{\text{JT}} = 170$ cm$^{-1}$ is obtained. $E_{\text{JT}}$ would thus be comparable to the spin-orbit coupling and smaller than the trigonal field $W$. This is incompatible with Ham's hypothesis ($E_{\text{JT}} \gg W, \lambda$). We must therefore deal with a case where the trigonal field is high.

The interaction of an electronic state $E$ (belonging to $C_{3v}$ symmetry) with vibration modes (belonging to $C_{3v}$ symmetry) is described in the mind of a cluster approximation or of an effective mode approximation we shall assume the coupling with one phonon mode of energy $\hbar \omega = 9$ meV.

We start with a vibronic hamiltonian:

$$
H_{\text{vib}} = T_N + \mathcal{V}_N + H_0 + H_{\text{EN}} + H_{\text{SO}}
$$

(4)

where $T_N$ is the kinetic energy of the nucleus, $\mathcal{V}_N$ is the potential energy of the nucleus (uncoupled with the degenerated electronic state $E$), $H_0$ is the electronic energy (the two-fold degenerated $E$ eigenvalue only is considered) $H_{\text{EN}}$ is the electron-nucleus coupling energy, $H_{\text{SO}}$ is the spin-orbit coupling energy. Taking into account the symmetry of the system [75], this hamiltonian can be written

$$
H_{\text{vib}} = T_N + \frac{1}{2} \mathcal{M}^2 (Q_2^2 + Q_3^2) I +
+ L (Q_a U_a + Q_b U_b) + \lambda' U_2 S_z
$$

(5)

where $(U_a, U_b)$ belong to an E representation of the $C_{3v}$ group and $U_2$ belongs to a $A_2$ representation of $C_{3v}$. $Q_a$ and $Q_b$ are mode partners belonging to an E representation of $C_{3v}$.

The unitary transformation:

$$
|a\rangle = \frac{1}{\sqrt{2}} \{ |+\rangle + |-\rangle \}
$$

$$
|b\rangle = \frac{1}{i\sqrt{2}} \{ |+\rangle - |-\rangle \}
$$

gives the same matricial form than used by Ham [74] for the operators associated with $E$ and $A_2$ representations for a doublet in cubic symmetric. This isomorphism allows us to apply Ham's theory for the $E \otimes \varepsilon$ problem in $C_{3v}$ symmetry. The main difference is that $U_2$ belongs to the $A_2$ representation of $C_{3v}$ and hence it can be subjected to a high reduction factor $p$ [74].

Assuming now a strong linear coupling ($L \gg \hbar \omega$ in equation (5)) the vibronic energy levels are [76]

$$
E = \hbar \omega \left( \nu + \frac{1}{2} \right) - E_{\text{JT}} + J^2 (\hbar \omega)^2 4 E_{\text{JT}}
$$

(6)

and the vibronic wave functions are approximately:

$$
|\Psi_J\rangle = \frac{1}{\sqrt{q}} X_J(q - q_0) X_J(\varphi) |\psi_\nu\rangle \quad \text{for} \quad L > 0
$$

and $|\psi_+\rangle$ for $L < 0$
\( \omega \) is the frequency of the mode, \( \nu \) is the radial quantum number, \( J \) is the rotational quantum number (in \( Q_a - Q_b \) space), \( E_{JT} \) is the Jahn-Teller Energy:

\[
L^2/8 \hbar \omega, X_j \text{ is the radial wave function centred in } q_0, X_j \text{ is the rotational wave function, } | \psi_+ \rangle \text{ and } | \psi_+ \rangle
\]

are the electronic wave functions obtained from \( | a \rangle \) and \( | b \rangle \) by an unitary transformation that separates the radial motion from the angular motion.

With that assumption (strong linear coupling) the ground state vibronic level \( | J | = 1/2 \) belongs to an \( E \) representation and the first excited level \( | J | = 3/2 \) is two-fold degenerated (\( A_1 + A_2 \)). A weak non linear coupling lifts that degeneracy and the distance between \( A_1 \) and \( A_2 \) is called \( \Delta' \). Voillot et al. [69] noticed that the \( I \) and \( J \) bands, corresponding to levels at 1.50 and 2.56 meV, had a rather large width and they suggested for them a vibronic origin (see Fig. 11).

The fine structure levels are fitted using the Hamiltonian

\[
H = \lambda' \sigma_x S_z + \mu(\sigma^- S^+ + \sigma^+ S^-) + \eta(\tau^+ S^{++} + \tau^- S^-) \tag{8}
\]

with

\[
\tau^+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \quad \text{and} \quad \tau^- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}
\]

each term of that Hamiltonian is invariant under time reversal [78].

If we set \( \mu \) and \( \eta \) equal to zero, we obtain five equally spaced levels. The distance between two levels is \( \lambda' \) and, in order to fit the experiment, \( \lambda' \) should be close to \( \pm 0.2 \) meV. The spin-orbit constant \( \lambda' \) is a reduced value of \( \lambda = 6 \) meV. \( \tau_z \) belonging to an \( A_2 \) representation, the reduction factor that we get is \( p = 0.03 \). This value is in very good agreement with the value obtained above from the vibronic structure.

To improve our description of the ground state, we can set non zero values to \( \lambda' \) and \( \eta \). If \( \lambda' = \pm 0.2 \) meV, \( \mu = 0.08 \) meV, a good fit is obtained for five levels but one level is not described. If we set \( \lambda' = 0.21 \) meV, \( \mu = 0 \) and \( \eta = 0.006 \) meV, we get a good fit for the six levels (see Fig. 11).

The third term \( (\tau^+ S^{++} + \tau^- S^-) \) can be obtained, not only from symmetry considerations, but also from a perturbation calculation. For example, the spin-orbit coupling gives to the second order of perturbation on the \( 5E \) level (coupling between \( 5E \) and \( 5A_1 \))

\[
H = \lambda' \sigma_x S_z + \mu(\sigma^- S^+ + \sigma^+ S^-) + \eta(\tau^+ S^{++} + \tau^- S^-) \tag{8}
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\]

each term of that Hamiltonian is invariant under time reversal [78].
the I and J levels as vibronic excited states. The same reduction factor $p$ is obtained from two independent experimental data:

- the energy difference $\Delta_1$ between the vibronic ground state and the barycentre of the states I and J,
- the fine structure splitting of the vibronic ground state.

4. Interpretation of the 0.574 eV, 0.535 eV system. — Reading again the results of Lightowlers et al. [5] on the 0.574 eV line, and the level diagram that they obtain it can be pointed out that the upper state fine structure of the 0.574 eV line could be, approximatively, superimposed to the ground state fine structure of the 0.839 eV line. Unfortunately the intrinsic line width of the 0.574 eV line does not allow to get all the details given by the 0.839 eV lines. These remarks, together with our experimental results lead us to interpret the 0.574 eV system as the complementary transition to the 0.839 eV band. That is to say:

$$\text{Cr}^{(2+ \text{ or } 0)}(C_{3v}) + \text{hole in the valence band} \rightarrow \text{Cr}^{(3+ \text{ or } +)}(C_{3v}) + h\nu = 0.574 \text{ eV}.$$ 

This would explain the width of the 0.574 eV lines and, on our assumption, the final state structure should correspond to the structure of a $d^3$ or $d^5$ ion in $C_{3v}$ symmetry ($d^3$ for $\text{Cr}^{3+}$ and $d^5$ for $\text{Cr}^+$ interstitial). The experimental results are in quite good agreement with the splitting predicted for a $\text{Cr}^+$ ion ($d^5$) in $C_{3v}$ symmetry. The spin hamiltonian is:

$$H = D [S_z^2 - \frac{1}{3} S(S + 1)]$$

and the $\text{Cr}^+$ level is splitted in three sublevels respectively separated by 2 $D$ and 4 $D$. That is experimentally observed with a $D$ value of 0.15 meV. This value is comparable to the value obtained for interstitial chromium coupled to an acceptor in silicon [70]. On our assumption, the best candidate is the interstitial chromium and so the 0.535 eV line, should be the transition (see Fig. 12a).

$$\text{Cr}^{0}(C_{3v}) \text{ (interstitial)} + \text{hole on the coupled acceptor} \rightarrow \text{Cr}^{+}(C_{3v}) + h\nu = 0.535 \text{ eV}.$$ 

Noticing, as Lightowlers et al. [6] did, that the ground state splitting is not very accurate we cannot affirm that our interpretation is the only possible. If there were only two levels, the interpretation in terms of $d^3$ ions would stand and the 0.535 eV line would be a transition to the $^4E$ coming from $^4T_1$ (see Fig. 12b).

The model that we have just described can be summarized by using the configuration-coordinate diagrams of the figure 12a and b. The ground state of the complexed chromium would be 0.574 eV above the valence band at 0 K. That gives for the excited $^5E^*$ level an approximative distance to the conduction band of 90 meV. Beside the characteristics of the luminescence bands that we have already explained, this diagram would explain that although the absorption at 0.839 eV line is very weak, the luminescence can be strong. That weak absorption is not due to a small

![Fig. 12. — Configurational coordinate diagram that could be expected : a) for chromium interstitial coupled to an acceptor; b) for a complex centre (Cr$_{3+}$-donnor).](image)
transition probability but rather to a small numbers of centres (\(10^{15}-10^{16}/\text{cm}^3\)). The rather high luminescence intensity can be explained either (substitutional case) by the attractive potential of the centre or (interstitial case) by the proximity of the excited state from the conduction band.

5. Interstitial or substitutional chromium. — Two possible complexes \((\text{Cr}^{2+}_\text{Ga}, X^-)\) or \((\text{Cr}^3+\text{Ga}, X^-)\) can very well explain the luminescence properties of GaAs : Cr.

If the substitutional model \((\text{Cr}^{2+}_\text{Ga}, (C_{3v}))\) logically proceeds of the known properties of chromium in GaAs, interstitial transition metal ions have never been observed, as far as we know, in II-VI or III-V compound. We wish to point out that this assumption is not unrealistic because in silicon, besides the fact they can be substitutional impurities, three transition metal ions (Fe, Mn, Cr) have been identified either as pure interstitial or as interstitial coupled with an acceptor (B, Al, Ga, In, Zn, Cu, Au). In the case of silicon, the transition metal ion is positively charged and the interaction is between opposite charges (as it is the case for substitutional impurities in a lot of materials [79]). The question is thus : will the chromium in GaAs have properties close to that of chromium in silicon? From the ionicity of Phillips [80], gallium arsenide lies between silicon and the II-VI compounds. From a steric point of view, there is no significant difference between silicon, GaAs and the zinc-blende II-VI's. So chromium in GaAs could have some properties comparable to chromium in the II-VI but also be close to chromium in silicon. Reminding that the limit solubility of chromium in GaAs is a few \(10^{17}/\text{cm}^3\), and that most of the semi-insulating GaAs : Cr crystals have concentrations close to that limit, it is possible to think, \textit{a priori}, that all other sites than the gallium site, and all sorts of associations (pairs, clusters...) will be enhanced if they represent a free energy gain.

In GaAs we think that, apart from chromium on gallium site (isolated) which is the predominant species [58, 81], a few other related defects could exist : \((\text{Cr}_{\text{Ga}}, X)\) complexes, interstitial chromium, \((\text{Cr}_1, X)\) complexes, and even chromium on arsenic site.

The existence of an interstitial chromium is coherent with the conclusion of Tuck et al. [62] who stated the possibility of an interstitial diffusion mechanism. As in silicon the interstitial diffusion mechanism is possible even at room temperature [70], in GaAs the interstitial chromium should be mobile at low temperature. A chromium interstitial coupled with an acceptor would be in agreement with our experiments and with the results of Brozel et al. [30] if that acceptor is silicon on an As site. Brozel et al. have shown that the solubility of chromium was enhanced by incorporation of silicon and they have found that silicon was both on Ga and As sites in that case.

The D.L.T.S. results of Houng et al. [82], who have found a hole trap at 0.58 eV from the valence band, can be explained by our interstitial model that gives a level at that depth, together with the out diffusion results of Tuck et al. [62]. Finally an isolated interstitial chromium \(\text{Cr}^+\) (in \(T_2\) symmetry) could explain the Cr isotropic signal at \(g = 1.993\) seen in most GaAs : Cr crystals under optical excitation.

On the other hand, the complexed substitutional model would better explain the small difference between 0.820 eV (isolated \(\text{Cr}^{2+}\)) and 0.839 eV (\(C_{3v} \text{Cr}^{2+}\)). Furthermore the presence of an impurity lowers slightly the \(\text{Cr}^{2+}\) state from 0.75 eV (isolated) to 0.58 eV (complexed) above the valence band, it should also lower the \(\text{Cr}^+\) state. This \((\text{Cr}^+, X^-)\) state should thus be just below the conduction band and that could explain the absence of 0.839 eV line in n-type material.

Thus till now we cannot rule out, any of the two possible models : \((\text{Cr}^{2+}_\text{Ga}, X^-)\) or \((\text{Cr}^3+\text{Ga}, X^-)\). Further studies and calculations will be necessary to choose between the two models.

6. Conclusion. — We have reminded in this paper that substitutional chromium in GaAs is a single acceptor and that the 0.839 eV line is not related to that centre. Then have been presented some new luminescence results on the 0.839 eV band and on the 0.574/0.535 eV system. In order to interpret the 0.839 eV data, we have proposed a model by introducing a \(C_{3v}\) symmetry by coupling a chromium atom (interstitial or on Ga site) to a nearest neighbor impurity. The group theory shows that such a symmetry explains both the high degeneracy and the 0.75 eV hump. A static description of the system gives a good quantitative agreement only for the excited \(5E^*\) state. In order to describe the ground state a vibronic hamiltonian has to be introduced. This description explains the shape of the I and J lines and gives a good quantitative agreement, for all the levels.

The 0.574 eV line is clearly associated to the 0.839 eV line and we interpret it as a transition from the chromium \((C_{3v})\) ground state towards the valence band. Our model is summarized on the configuration coordinate diagrams of the figure 12. The existence of interstitial chromium would explain many other properties of chromium in GaAs diffusion, hole trap in epitaxies, \(\text{Cr}^{+}\ E.S.R.\) signal, but we cannot still choose between the two models : \((\text{Cr}^{2+}_\text{Ga}, X^-)\) and \((\text{Cr}^3+\text{Ga}, X^-)\).

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[78] The effective hamiltonian \( H = \eta (s^+ S^+ + s^- S^-) \) is invariant under time reversal because \( s^+ \) and \( s^- \) come from a second order perturbation theory so that under time reversal \( s^- \rightarrow s^+ \) and \( s^+ \rightarrow s^- \).


