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YAG photoluminescence of GaAs : Cr (*)

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Résumé. — Nous avons étudié en photoluminescence une série d'échantillons de GaAs dopés chrome. Deux sources d'excitation ont été utilisées : un laser YAG et un laser krypton. La concentration en porteurs libres des échantillons est comprise entre 10^{18} cm^{-3} (type n) et type p (faiblement dopé). Trois bandes de photoluminescence sont attribuées au chrome : 0,57 eV, 0,61 eV et 0,839 eV. Nous présentons leurs variations respectives en fonction de la source d'excitation et de la position du niveau de Fermi. Nous proposons un modèle, en termes de coordonnée de configuration, qui pourrait expliquer la plupart des propriétés observées.

Abstract. — We have performed photoluminescence experiments, using two excitation sources : a YAG laser and a krypton laser, on a series of Chromium doped GaAs samples. The carrier concentration of the samples ranges from 10^{18} (n-type) to p-type (lightly doped). Three bands of photoluminescence at 0.57 eV, 0.61 eV and 0.839 eV are associated with Chromium. Their respective variations with excitation source and Fermi level position are reported. A tentative explanation in terms of the Configurational-Coordinate model for the $(\text{Cr}^{3+}-\text{Cr}^{2+})$ centre is presented.

1. Introduction. — Due to the increasing use of chromium-doped semi-insulating substrates of Gallium Arsenide, and due to the problems related to that material (thermal stability [1], Chromium exodiffusion [2]...), a lot of studies have been performed on chromium in GaAs by different methods. Among these, photoluminescence has been very widely used [3-11] because chromium related photoluminescence is easily observed. The 0.839 eV line has been the subject of a great deal of papers and the outstanding opinion is that this luminescence is due to an internal transition ($^5E-^5T_2$) of the Cr^{2+} centre.

Our attempt has been to correlate absorption under hydrostatic pressure, EPR and photoluminescence measurements on a series of chromium doped samples having a varying free carrier concentration. We publish here the results of the photoluminescence experiments and a tentative interpretation of some of the data. Results of other experiments will be published also in this issue [12].

2. Samples. — Two types of samples have been studied. At first, samples doped with chromium during

the growth process. These samples are semi-insulating with a chromium concentration ranging between a few 10^{15} cm^{-3} and a few 10^{17} cm^{-3} . They come from different manufacturers : RTC (80, 123, 217, 399, 400, 420), Sumitomo (FS 20344) and Metal Research. For comparison, semi-insulating samples without chromium have been also tested.

The second kind of samples is obtained by diffusion. Chromium was evaporated on both faces of a slice of n-type GaAs (Te doped $n \sim 10^{18}$) and then diffused during one or a few days in a quartz ampulla at different temperatures. For $T < 1100^\circ\text{C}$, n-type samples of GaAs : Cr were obtained whereas for $T > 1100^\circ\text{C}$, semi-isolated or p-type samples were obtained. Both faces of the samples are then polished, removing a thickness of about 200μ from each side. After this treatment, followed by chemical etching, the samples were found optically homogeneous.

3. Experiment. — The photoluminescence set up has the following characteristics. Detection is made using a cooled PbS cell, the monochromator has a focal length of 1 m and the sample temperature can be varied between 4 K and 300 K. We have used two excitation sources : a krypton laser with a power of 1 W at 0.647μ (1.92 eV, over-gap excitation) and a YAG laser, 1.5 W at 1.06μ (1.17 eV, under-gap excitation). The photoluminescence spectra are cor-

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rected for filter, lens and grating transmission and PbS cell spectral detectivity.

4. Results. — The results that we obtain depend both on the Fermi-level position in the sample and on the excitation source used. The 0.839 eV band is very easy to recognize due to its zero-phonon line. The identification is far more difficult for the bands appearing in the range 0.5 to 0.7 eV. After a fine analysis of all the data it seems to us that four bands exist at 0.57, 0.61, 0.64 and 0.68 eV, each of them having a width at 4 K greater than 100 meV. Therefore, if two or more of these bands are present in the sample at the same time, we will only see one band of different shape.

In order to analyse the results, we fit the corrected curves with gaussians. This type of fit gives good results except for the 0.57 eV band which is clearly non-symmetrical. In that case, the curve can be correctly fitted, following the Huang-Rhys model [13], by the law

$$I(h\nu) = I_0 \exp(-S) \frac{S \left(\frac{E_i - h\nu}{\hbar\omega} \right)}{\left(\frac{E_i - h\nu}{\hbar\omega} \right)!}$$

where E_i is the thermal energy of the level, $\hbar\omega$ the energy of the involved phonon and S the mean number of emitted phonons.

Table I summarizes the results of the fit. YES means that we have used the corresponding band to obtain the best fit. It is clear that 3 bands at 0.57, 0.61 and 0.839 eV appear only in Chromium doped samples whereas the two other at 0.64 and 0.68 eV appear also in semi-insulating samples without Chromium.

Table I.

Excitation Sample	YAG laser				Krypton laser		
	0.57	0.61	0.68	0.839	0.57	0.64	0.839
Cr ¹ : 10 ¹⁸ cm ⁻³	NO	YES	NO	NO	NO	YES	NO
Cr ² : 4 × 10 ¹⁷ cm ⁻³	NO	YES	NO	NO	YES	YES	YES
SI low Cr	YES	NO	NO	NO	YES	YES	YES
SI high Cr	YES	NO	NO	YES	Weak	Weak	YES
Cr ⁸ : p-type	YES	NO	NO	YES	YES	YES	YES
SI : no Cr	NO	NO	YES	NO	NO	YES	NO

5. Discussion. — The origin of the 0.64 eV (krypton) and 0.68 eV (YAG) bands might be oxygen or some oxygen-induced centre [15] because :

— they appear very strongly in semi-insulating material grown without Chromium but with Ga₂O₃ added to the melt,

— their energy correspond quite well to the energy given for the « O » centre and the Franck-Condon shift that we obtain : 100 meV is close to the shift given by Bois *et al.* [14].

Unfortunately, it is very difficult to measure chemically the oxygen concentration in GaAs and we have not yet been able to correlate the presence of these levels to the oxygen content of our samples.

We will now associate the three bands 0.57, 0.61 and 0.839 eV to the Chromium doping and discuss their properties. First of all, the 0.839 eV line, has been clearly related to Chromium in a number of papers but :

— The zero-phonon-line structure [9] does not agree with the ground state ⁵T₂ splitting obtained from EPR measurements.

— In many samples, especially in n-type ones, of GaAs : Cr, there is no quantitative agreement between the Cr²⁺ EPR signal and the 0.839 eV luminescence band.

Although this band is clearly an internal transition in some centre, it cannot be related to the ⁵E-⁵T₂ transition in Cr²⁺.

The figure 1 shows the 0.61 eV band. The spectrum from a $n = 4 \times 10^{17}$ sample excited by the YAG laser is fitted using the following values :

$$E_0 = 0.615 \text{ eV} \quad \text{and} \quad W = 132 \text{ meV}.$$

Fig. 1. — Best fit of the spectrum of Cr² sample ($n = 4 \times 10^{17} \text{ cm}^{-3}$) excited with a YAG laser. The maximum is at $E_0 = 0.615 \text{ eV}$ and the width of the gaussian is 132 meV. (+) : experimental points, (-) : theoretical curve.

This band only appears with YAG laser in n-type samples. With krypton light it is hidden by the 0.64 eV band which is much more intense. This band appears

only on Chromium doped samples and is present in samples where the EPR signal of Cr^{2+} is stable and the EPR signal of Cr^{3+} absent.

The 0.57 eV band (Fig. 2) appears with YAG laser in semi-insulating or p-type Chromium doped samples. With krypton laser, this band is weaker and is mixed with the 0.64 eV band but it can be detected in most of the samples. This band exists when Cr^{3+} (EPR) is present in the sample. It is not symmetrical and it has been fitted, as explained earlier, using the Huang-Rhys model. The fit cannot give us the 3 parameters (E_t , $\hbar\omega$, S) but if we take the Franck-Condon shift ($d_{\text{FC}} = S\hbar\omega$) measured by Hennel *et al.* [12] and Kocot *et al.* [4] : 170 meV, we obtain $E_t = 0.72$. If we take the value $E_t = 0.76$ eV obtained by Hennel *et al.*, we find $d_{\text{FC}} = 210$ meV. The agreement is quite good and we are therefore tentatively propose a configurational coordinate model that could explain some of the properties of Chromium in GaAs.

Fig. 2. — Best fit of the 0.57 eV band in SUMITOMO FS 20344 sample. The following parameters have been used (see text) $E_t = 0.76$ eV, $\hbar\omega = 15$ meV, $S = 14.3$ ($d_{\text{FC}} = 210$ meV). (+) : experimental points, (—) : theoretical curve.

The model is shown on figure 3. The 0.57 eV band corresponds to a transition between the (Cr^{2+} - Cr^{3+}) level and the valence band and the 0.61 eV band to a transition between the conduction band and the (Cr^{2+} - Cr^{3+}) level. (Cr^{2+} - Cr^{3+}) means the Chromium acceptor level which is in the state of charge Cr^{3+} when empty and in the state Cr^{2+} when filled.

From this model it can easily be explained that the 0.57 eV band is seen with YAG laser when Cr^{3+} is present in the sample. The absorption of light by the transition Valence-band $\rightarrow \text{Cr}^{2+}$ is very efficient in the energy range of the laser. So we fill the empty

places of the centre, and the electrons return to thermal equilibrium by emitting a photon of 0.57 eV.

When all (Cr^{2+} - Cr^{3+}) centres are filled, as in n-type samples, we can only make transitions to the conduction band with the laser. The further recombination gives rise to the 0.61 eV band. With krypton laser, the same phenomena occur except that they are masked by the 0.64 eV luminescence.

We can also explain in that model why the internal transition (5E - 5T_2) in Cr^{2+} should not be seen. The 5E state is degenerated with the conduction band [16, 17] and therefore, the transition to the Cr^{2+} level are more probable from the bottom of the conduction band. The DLTS results [18] are also in reasonable agreement with the thermal values given by our model.

6. Conclusion. — Our experiments suggest that the 0.64 and 0.68 eV bands are not related to Chromium. The 0.839 eV band is related to Chromium, it is an internal transition but it is not the (5E - 5T_2) transition in Cr^{2+} . The 0.57 eV and 0.61 eV band are the transition between the (Cr^{2+} - Cr^{3+}) level and the valence band and conduction band respectively. The model that we propose agrees quite well with other experiments and it explains why the internal transition (5E - 5T_2) in Cr^{2+} was not observed.

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Fig. 3. — Tentative model for the (Cr^{3+} - Cr^{2+}) acceptor centre. The thermal energy of the level with respect to the valence band is 0.76 eV. The Franck-Condon shift is 170 meV. The absorption and emission energies are indicated. In the Cr^{2+} charge state, exists an excited level (5E) which is degenerated with the conduction band.

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