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Cr^{2+} INTERNAL LUMINESCENCE IN GaAlAs.

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Chromium related luminescence has been studied in GaAlAs (11 % < Al < 38 %) doped by chromium diffusion at 900°C. A luminescence band centered around 0.78 eV is obtained. This band is shown to be of a different nature from the 0.839 eV band in GaAs:Cr, related to a Cr^{2+} - Donor complex, and is shown to be quite similar to the luminescence band observed in GaAs:Cr under hydrostatic pressure. We interpret that luminescence as an internal transition ^5E - $^5T_2$ in isolated Cr^{2+} ions. The transition is possible because the ^5E state is in the forbiden gap for Al > 11 %. The fit of the luminescence spectrum leads us to assume the spin orbit coupling to be weak, that is explained by comparison with ZnSe.

INTRODUCTION

The well known 0.839 eV luminescence line in GaAs:Cr has long been attributed to the internal (^5E - $^5T_2$) d.d transition of Cr^{2+} on gallium site [1]. White [2] and Deveaud et al [3] have shown that this attribution could not stand ; a further reason was given by the observation of the absorption zero phonon line of the Cr^{2+} transition at 0.820 eV [4], agreing with E.P.R. results. Picoli et al [5,6] have then proposed a model to explain the 0.839 eV luminescence. The band is associated to an internal transition of a Cr^{2+}- Donor first neighbour complex (C_{3v} symmetry) which is thought to involve less than 5 % of the total amount of chromium in the lattice. This model has been confirmed by Zeeman experiments [7].

Transitions between the isolated chromium and the bands have been observed in GaAs under YAG laser excitation [3], but no luminescence band can be associated with a Cr^{2+} internal transition. As this was stated in [3], the explanation could be the fact that the ^5E excited state of Cr^{2+} is in resonance with the conduction band. This resonance was proved either by the fact that the Cr^{2+} internal absorption band was also observed in photoconductivity [8] or by a simple energy difference argument : the zero phonon line is observed in absorption at .82 eV and the ground state is 0.78 eV below the conduction band edge at OK [9,10]. Thus, the ^5E state should be 40 meV above the conduction band minimum. The 0.82 eV Z.P.L. has recently been observed in photoconductivity [11] which confirms that the ^5E state is resonant with the conduction band.

The ^5E - $^5T_2$ luminescence would only be observed if the ^5E state was in the band gap. Kocot et al [12] have demonstrated by photoconductivity measurements that the ^5E level was crossing the conduction band edge for an Al concentration around 15 % at 80 K. At 4 K, the crossing point should occur for lower Al compositions. Hennel et al [9] have shown that this crossing could be obtained by applying an hydrostatic pressure of about 6 K bar. So, the Cr^{2+} internal luminescence can be though to appear either in $Ga_{1-x}Al_xAs$: Cr for x > 15 % or in GaAs:Cr for hydrostatic pressures above 6 K bar. This work presents the results obtained on GaAlAs:Cr, the results obtained when applying hydrostatic pressure will be published elsewhere [13].

EXPERIMENT

$Ga_{(1-x)}Al_xAs$ epitaxial samples (11 % > x > 38 %) where kindly given by Mr VARON (RTC CAEN). We have worked on 20 µ thick L.P.E. layers grown on GaAs substrates without Cr doping. The Cr diffusion was performed at low temperature : 900°C, 15 min, the sample being coated with a Si_3N_4 layer. Such a temperature is high enough to get a few 10^{16} cm^{-3} chromium ions in the first microns and low enough to avoid destroying the surface quality. It is not possible to work at higher temperatures because of surface degradation.

The luminescence is excited with an argon laser so only the first micron of the sample is excited and no GaAs related luminescence was detected. Although reduced by chromium diffusion, the Donor Acceptor pair transition of GaAlAs stays at the same energy position, we therefore think that our technological process does not alter the composition of the alloy.

RESULTS AND DISCUSSION

All chromium diffused layers that we have measured show, (after diffusion only), a broad band centered around 0.78 eV (see figure 1) which does not appear in GaAs when diffused in the same conditions. This luminescence band has to be compared with the 0.839 eV band in GaAs:Cr. The former does not present any zero phonon line, and its width is much larger so that they cannot be confused. Furthermore, the shape of that band and its position correspond very well to what is observed in GaAs:Cr under high hydrostatic pressure [12], when observed at the same temperature.

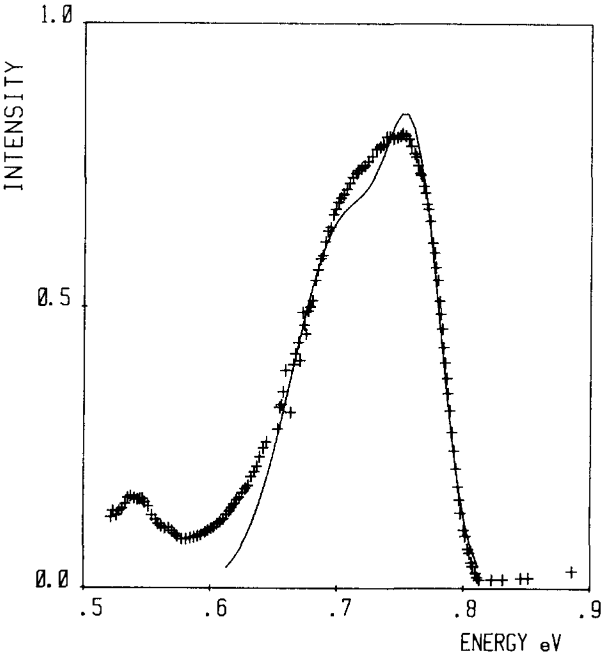

Figure 1 : Luminescence of a chromium diffused $Ga_{1-x}Al_xAs$ (Al = 24%) epitaxial layer.

The crosses correspond to the experimental points at T = 4.2 K and the solid line to theoritical fit using Kaminska et al [14] model ($\lambda = 0$ cm^{-1}, E_{JT} ($^5T_2$) = 600 cm^{-1}, and E_{JT} (^5E) = 40 cm^{-1}).

We thus interpret the luminescence band that we observe as being due to an internal transition of isolated $Cr^{2+}{}_{Ga}$ in GaAlAs. This transition can be observed because the ^5E state is below the conduction band edge (see figure 2). Our measurements show that the crossing occurs before 11 % which is the lowest Al concentration that we have studied. This crossing point is close to the point obtained by Kocot et al [13].

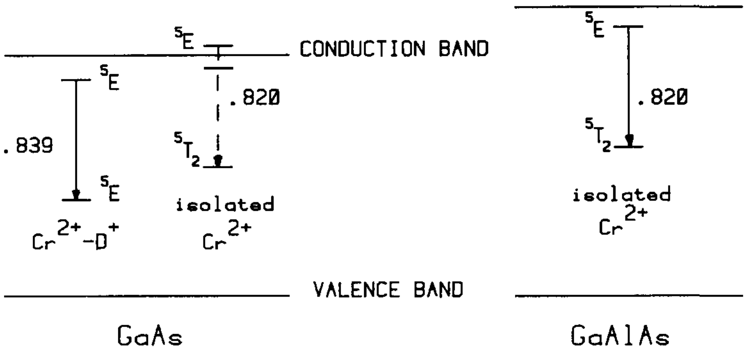

Figure 2 : Schematic band diagram of GaAs and GaAlAs showing why the $Cr^{2+} - D^+$ emission is observed in GaAs, the Cr^{2+} emission in GaAlAs but not in GaAs. The $Cr^{2+} - D^+$ emission cannot be observed in GaAlAs because it is too weak compared to the isolated Cr^{2+} emission.

Following the work of Kaminska et al [14], we have tried to fit the experimental spectra. As the band only shows two humps, we have been led to assume the spin orbit coupling constant λ to be very weak in the ground state, as did Kaminska et al [14] for ZnSe:Cr. In fact, the properties of Cr^{2+} ions are very close in GaAs and ZnSe, this is thought to be due to the closely related properties of the two compounds. The near zero λ value can be obtained from the interpretation of the parameters of the effective spin Hamiltonian which describes the E.P.R. results [15]. A Ligand field model has been developed to account for the fine structure parameters. Their large variations from one II-VI compound to another are explained by the variations of the spin orbit constants of the ligands. A low value of λ can be expected for Cr^{2+} in GaAs, as in ZnSe, for two main reasons :

i) the experimental fine structure parameters in the effective E.P.R. hamiltonian of Cr^{2+} are very close in GaAs and ZnSe.

ii) the spin orbit constants of the ligands As and Se are similar, as are the overlap coefficients related to the ligand effect.

When introducing a zero λ constant, the calculation of Kaminska et al is very easy and does not need lengthy computer calculations. The luminescence spectrum is described in the following manner : the initial state ^5E is submited to a weak Jahn-Teller effect E_{JT} (^5E) and the final state $^5T_2$ to a strong Jahn-Teller E_{JT} ($^5T_2$). The transition probability is written in the Born-Oppenheimer approximation : the wave functions of the initial and final states are the product of an electronic and a vibrational part. We then use the semi-classical approximation : the transition occurs at Q_θ, Q_ε constant and the initial state is weighted by the Bolzman factor. Then are introduced the electronic matrix elements that we suppose always equal to 1. This is a crude approximation but in a dynamic state, we should have vibronic wave functions of ^5E symmetry and all transitions should be allowed.

Finally, we have obtained a rather good fit of the experimental results (see figure 1) by using that procedure and the following parameters :

$$E_{JT}\ (^5T_2) = 600\ cm^{-1}\quad ,\quad E_{JT}\ (^5E) = 40\ cm^{-1}.$$

These values are in reasonable agreement with the values that can be expected from comparison both with absorption in GaAs and with optical results in ZnSe:Cr.

CONCLUSION

We have been able to observe the Cr^{2+} internal transition by diffusing chromium in GaAlAs layers of different compositions. That luminescence cannot be observed in GaAs because the ^5E state is resonant in the conduction band. That interpretation is consistent with earlier results on GaAs:Cr and with the published results in the II-IV compounds. We find that the spin orbit coupling constant is very weak in the ground state and a first attempt to fit the luminescence data gives as Jahn-Teller energies : 600 cm^{-1} in the ground state and 40 cm^{-1} in the excited state.

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