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$Cr^{2+}(3d^4)$ ABSORPTION IN GaAs*

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We report the observation of the zero-phonon structure of the 0.9 eV absorption in GaAs : Cr, which correspond to intracenter Cr^{2+} transition. This result and the existence of the stable Cr^{2+} state in our *n*-type GaAs : Cr samples, allow to consider that Cr^{2+} is the dominant chromium state in these crystals.

IT IS WELL KNOWN that in GaAs single crystals the three charge states $Cr^{3+}(3d^3)$, $Cr^{2+}(3d^4)$ and $Cr^{1+}(3d^5)$ of substitutional chromium impurity can be observed by Electron Paramagnetic Resonance (EPR) [1], but in spite of the large number of published papers there is no clear correlation between the optical properties of chromium impurity in GaAs and its different charge states.

For instance the 0.839 eV luminescence and absorption of GaAs : Cr is interpreted as intracenter Cr^{2+} transition [2, 3], although the observed zero-phonon lines do not correspond with the Cr^{2+} ground state structure found in EPR [1].

An absorption broad band at 0.9 eV was reported [4–6] in *n*-type GaAs. This band was also interpreted [5, 6] as intracenter Cr^{2+} transition, but its zero-phonon structure has not been observed even at liquid helium temperature [4]. Furthermore some authors state that in *n*-type GaAs only Cr^{1+} state exists [7, 8] although the Cr^{2+} signal was observed in EPR in *n*-type samples [9].

In this communication we show that Cr^{2+} is the dominant chromium state in *n*-type GaAs : Cr, and that its zero-phonon absorption structure exists at an energy of 0.82 eV and corresponds very well with EPR results.

We have performed magnetic resonance and optical absorption measurements on *n*-type GaAs : Cr obtained by diffusion of chromium into *n*-type GaAs : Te($n \simeq 10^{18}$ cm^{-3}) [10]. The magnetic resonance spectrum exhibits several features:

(i) a cyclotron resonance signal of conduction electrons;

(ii) a Cr^{2+} EPR signal non sensitive to 1.09 μm argon laser illumination;

(iii) Cr^{1+} and Fe^{3+} EPR signals which are growing under 1.09 μm argon laser illumination.

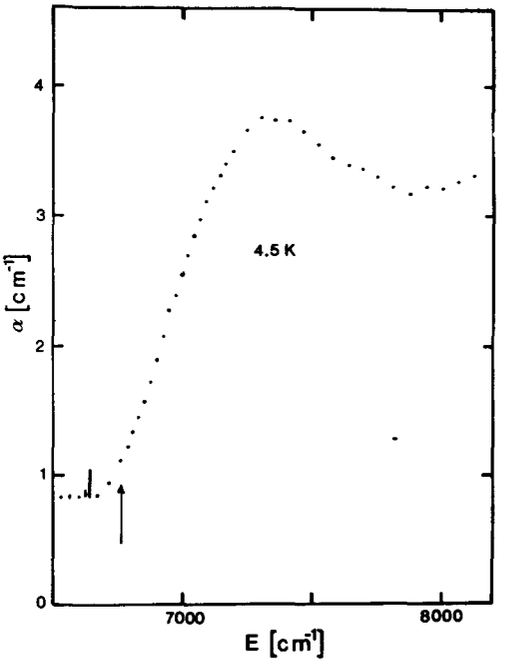

Fig. 1. Intracenter Cr^{2+} absorption band ($^5T_2 \rightarrow {}^5E$) with its zero-phonon lines. The arrow shows the position of the zero-phonon lines observed by Lightowlers *et al.*

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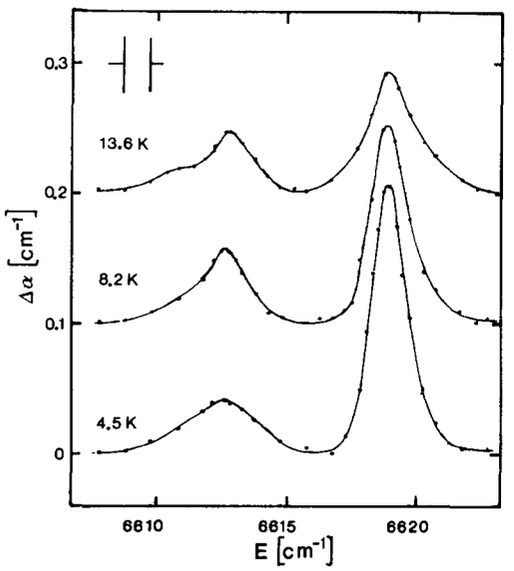

Fig. 2. Absorption due to zero-phonon lines at three different temperatures; the raising of the third line in the lower energy side can be observed. The slitwidth is 1 cm^{-1}. For 8.2 and 13.6 K the absorption curves are shifted towards higher absorption respectively by 0.1 and 0.2 cm^{-1}

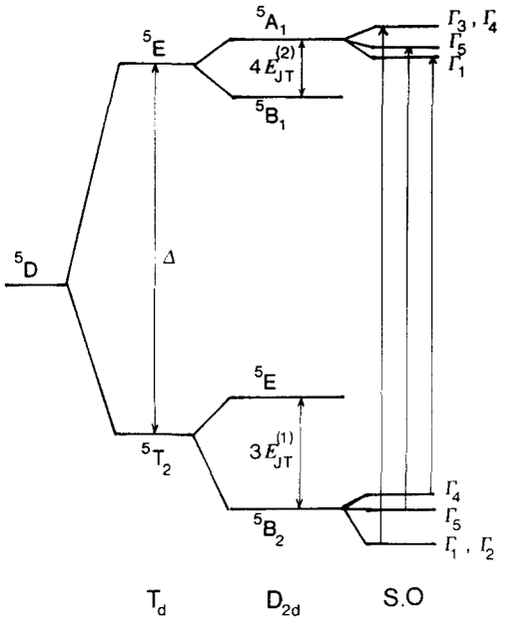

Fig. 3. Level scheme of ^5D state of Cr^{2+} ion in GaAs, the dipolar electric allowed optical transitions are represented by arrows.

This last feature, encountered in all samples we made whatever is their type, will be discussed in a further publication [10].

In the optical absorption experiments, we observe the 0.9 eV band previously reported [4–6]; we also observe two weak zero-phonon lines at 4.5 K (Figs. 1 and 2). The main line is at 6619 cm^{-1}, and the weaker one 6.5 ± 0.3 cm^{-1} lower in energy. With the increasing temperature one can observe an intensity transfer between these lines, and a third weak line which appears at about 8.5 cm^{-1} from the main line towards low energies. It should be noticed that the absorption structure which was interpreted as Cr^{2+} intracenter transition by Lightowlers *et al.* [3] exists at energy 0.839 eV (6770 cm^{-1}), i.e. about 150 cm^{-1} higher in energy that the lines we observe and cannot correspond to zero-phonon lines of the 0.9 eV band (Fig. 1).

The observed zero-phonon structure and its temperature dependence can be explained with the help of the $Cr^{2+}(d^4)$ ground state ($^5T_2$) splitting determined by EPR [1]. The $^5T_2$ state is suffering a tetragonal Jahn–Teller distortion and is split into $^5B_2$ and ^5E levels [1] (Fig. 3). The ground $^5B_2$ level is further split (for instance by spin-orbit coupling) into four levels Γ_1, Γ_2, Γ_5 and Γ_4. The Γ_1–Γ_2 splitting a_{B_2} = 0.031 cm^{-1} can be neglected at the scale of an optical experiment as well as the quartic axial field F_{B_2} (which has also been neglected in [1]). With these approximations, the Γ_1, Γ_2–Γ_5 splitting is equal to $3D_{B_2} = -5.6$ cm^{-1} and the Γ_5–Γ_4 splitting is $D_{B_2} = -1.9$ cm^{-1}.

If the excited state ^5E was not subjected to Jahn–Teller effect, one should observe 7 zero-phonon lines in absorption [11]. If one consider also a Jahn–Teller distortion in the excited state (such effect exists in the excited state of Cr^{2+} in II–VI compounds [12]), the ^5E state is split into $^5A_1$ and $^5B_1$ levels (Fig. 3). It is important to note that only the $^5B_2(^5T_2) \rightarrow {}^5A_1$ (^5E) transition is dipolar electric allowed. The $^5A_1$ state is further split into Γ_1, Γ_5, Γ_3 and Γ_4 levels. If one make the same approximations as in the ground state, the Γ_3, Γ_4–Γ_5 splitting is equal to $3D_{A_1}$ and Γ_5–Γ_1 splitting is equal to D_{A_1}. The dipolar electric allowed transitions are shown in Fig. 3. In such a case, one should observe at high temperature three lines split by $3(D_{A_1} - D_{B_2})$ and $(D_{A_1} - D_{B_2})$. This situation corresponds exactly to what is observed. From the experimental values, we deduced D_{A_1} = (+ 0.3 ± 0.1) cm^{-1}. The temperature dependence of the line intensities can be also explained considering the thermal population of the ground state levels (Fig. 3).

The obtained energy difference between the zero-phonon lines and the maximum of the absorption band $\Delta E \simeq 700$ cm^{-1}, allows to estimate the Jahn–Teller energy (E_{JT}) in the $^5T_2$ state. In the case of the same phonon energy for the ground and excited states one obtains

$$\Delta E = \left(1 - \frac{V_2}{V_1}\right)^2 E_{JT} \quad (1)$$

where V_1 and V_2 are the coupling coefficients of the lattice to the orbital $^5T_2$ and ^5E states respectively. If we make the rough approximation

$$0 \leqslant -\frac{V_2}{V_1} \leqslant 1 \quad (2)$$

the limits of which correspond to the cases where there is no Jahn–Teller coupling in the ^5E state, or where its absolute value is as strong as the one in the $^5T_2$ state, it is easy to obtain from equations (1) and (2)

$$175\ \text{cm}^{-1} \leqslant E_{JT} \leqslant 700\ \text{cm}^{-1} \quad (3)$$

for $\Delta E = 700\ \text{cm}^{-1}$.

The lower energy limit corresponds to the value of the ratio of the intensities of the zero-phonon lines to the absorption band [11] $\alpha_L \simeq 10^{-3}$, the higher energy limit to $\alpha_H \simeq 5 \times 10^{-5}$. These values were calculated for TA phonon energy $E_p = 70\ \text{cm}^{-1}$, according to the results obtained for Cr^{2+} in II–VI compounds [12]. The fact that the experimental value $\alpha_{exp} \simeq 3 \times 10^{-4}$, is between these two limits suggests that the estimation (3) is reasonable and that the value proposed by Krebs and Stauss [13] ($E_{JT} = 1500\ \text{cm}^{-1}$) is probably too large.

It should be mentioned that similar zero-phonon structure of Cr^{2+} was observed by Kaufmann *et al.* [14] in GaP, by Vallin *et al.* [11] in ZnSe and by Grebe and Schulz in ZnS [15].

In conclusion we want to stress that Cr^{2+} charge state in GaAs is stable in *n*-type crystals and that the zero-phonon structure at 0.839 eV observed in luminescence and absorption [2, 3] by several authors is undoubtedly connected with chromium but not directly with substitutional Cr^{2+} intracenter $^5T_2 \rightarrow {}^5E$ transition. The interpretation of this very complex structure is still open to discussion.

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