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Photoionization transition $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ in GaAs : Cr ⁽¹⁾ ⁽³⁾

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Résumé. — Le spectre d'absorption de photoionisation d'échantillons de GaAs fortement dopés au chrome a été mesuré dans la région d'énergie comprise entre 5 500 et 11 000 cm^{-1} jusqu'à une pression de 9 kbar à 300 K et 77 K. Les mesures de RPE sous excitation optique (1,09 μm) montrent que cette absorption est due à un transfert de charge de Cr^{3+} vers Cr^{2+} . Un modèle théorique tenant compte de la relaxation de réseau est utilisé pour reproduire les courbes de photoionisation. Les valeurs d'ionisation optique E_O et thermique E_T ainsi que leur dépendance en fonction de la pression sont obtenues. On trouve une énergie de relaxation $E_R = E_O - E_T$ de l'ordre de 0,17 eV et une section efficace de capture pour l'absorption d'environ $5 \times 10^{-17} \text{cm}^2$.

Abstract. — The photoionization absorption spectrum of the strongly Cr-doped GaAs samples was measured in the energy region 5 500-11 000 cm^{-1} under hydrostatic pressure up to 9 kbar at 300 K and 77 K. The EPR measurements with 1.09 μm laser excitation shows that this absorption is due to the charge transfer $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ transitions. The theoretical model which takes into account the lattice relaxation effect is used to fit the photoionization absorption curves. The values of optical ionisation energy E_O , thermal ionization energy E_T and their pressure dependence are obtained. The relaxation energy $E_R = E_O - E_T$ is found as about 0.17 eV and the absorption cross section as about $5 \times 10^{-17} \text{cm}^2$.

1. Introduction. — It is well known that bulk semi-insulating GaAs doped with chromium possess a broad absorption band which begins at about 0.8 eV and runs up to the fundamental absorption edge (1.4 eV) [1, 2, 3]. This absorption was qualitatively attributed to the optical transition of electrons from the valence band to a chromium acceptor level located in the middle of the energy gap i.e. to the $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ transition. The shape of the band and its variation with temperature were not yet understood.

This paper presents results of measurements of this absorption at different temperatures and under pressure together with a detailed analysis which brings a quantitative information about the chromium acceptor level.

2. Experimental procedure. — Two types of GaAs : Cr samples were measured, RT 123 Cr doped in liquid phase and p-type sample (Cr 8) doped with chromium by diffusion [4, 5]. The samples were optically polished. The absorption measurements were performed under vacuum with a grating spectrometer and a PbS detector at room and liquid nitrogen temperatures. Pressure was applied hydrostatically through the compression of He gas up to 9 kbar at both temperatures.

For Cr 8 sample, the EPR spectrum with 1.09 μm argon laser excitation was also measured.

3. Identification of the optical transitions. — The absorption spectrum of both samples in the energy region 5 500 cm^{-1} -11 000 cm^{-1} at room temperature is shown in figure 1. It is easy to observe that in both cases one has to deal with the same type of absorption, but the number of active centres is a few times smaller in the semi-insulating sample.

Part of the EPR spectrum of p-type sample is shown in figure 2. It is similar to that published by Krebs and Stauss [6, 7]; the Cr^{3+} and Cr^{2+} lines

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Fig. 1. — The GaAs : Cr absorption coefficients at room temperature for the Cr 8 sample (empty dots left scale) and the RT 123 sample (full dots right scale). The solid lines are drawn according to formula (1) for $E_0 = 7\,500\text{ cm}^{-1}$, $\Gamma = 1\,125\text{ cm}^{-1}$.

can be observed. Under the $1.09\text{ }\mu\text{m}$ argon laser excitation the Cr^{2+} spectrum is decreasing by about 20 % and Cr^{2+} line is growing by about one order of magnitude. It is worth noticing that the laser energy ($9\,170\text{ cm}^{-1}$) corresponds to the maximum of the absorption spectrum. This fact and the quantitative properties of the EPR spectrum under illumination allows to state finally that the observed absorption is due to $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ charge transfer as it was suggested previously [3].

Fig. 2. — EPR spectrum of Cr 8 sample obtained with and without the $1.09\text{ }\mu\text{m}$ argon laser illumination. The observed effects are reversible.

One can also estimate the numbers of Cr^{3+} centre in the measured samples with the help of Martin's *et al.* calibration [3]. These authors showed that at room temperature, $\Delta\alpha = 1\text{ cm}^{-1}$ at $1.35\text{ }\mu\text{m}$ corresponds to a number of chromium centre

$$N_{\text{Cr}} = 5.7 \times 10^{16}\text{ cm}^{-3}.$$

In our case $\Delta\alpha = 1.4\text{ cm}^{-1}$ for RT 123 sample and 9.8 cm^{-1} for Cr 8 sample, these values lead to

$$N_{\text{Cr}} = 8 \times 10^{16}\text{ cm}^{-3}$$

and $5.6 \times 10^{17}\text{ cm}^{-3}$ respectively.

4. Temperature dependence of the absorption spectrum. — The absorption spectrum of p-type sample in liquid nitrogen temperature is presented in figure 3.

Fig. 3. — The GaAs : Cr (Cr 8) absorption at liquid nitrogen temperature for $P = 1\text{ bar}$ (empty dots) and $P = 9\,250\text{ bar}$ (full dots). The solid lines are drawn according to formula (1) for $E_0 = 7\,525\text{ cm}^{-1}$ and $7\,675\text{ cm}^{-1}$ respectively.

The absorption edge between $7\,000$ and $8\,000\text{ cm}^{-1}$ is sharpened and a maximum at $9\,300\text{ cm}^{-1}$ arrives. This fact cannot be explained without taking into account an impurity-lattice relaxation process after the $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ transition. In a simple model which is presented in figure 4, one expects that an

Fig. 4. — Configuration coordinate diagram for $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ transition. E_0 : optical energy, E_T : thermal energy, $E_R = E_0 - E_T$: relaxation energy.

optical transition which begins at energy E_0 is broadened by impurity-lattice interaction, which changes the distance Q between the impurity and its ligands.

To calculate the shape of the absorption the model proposed by Kopylov and Pikhtin [8] in its semi-classical form, with two independent parameters introduced by Piekara *et al.* [9] was used. In this model the absorption cross section for a band to level allowed transition is described with the following formula :

$$\sigma = \sigma_0 \frac{E_0^{5/2} \Gamma^{1/2}}{(\hbar\omega)^3} \int_{-\beta}^{\infty} \frac{(\beta + z)^{1/2} \exp(-z^2)}{1 + \left(\frac{\Gamma z}{\hbar\omega}\right)^2} dz. \quad (1)$$

Where E_0 is the optical energy and Γ the broadening parameter given by :

$$\Gamma = \Gamma_0 \coth^{1/2} \left(\frac{\hbar\omega_0}{2kT} \right) = \sqrt{2 \hbar\omega_0 (E_0 - E_T) \coth \frac{\hbar\omega_0}{2kT}}$$

$$\beta = \frac{\hbar\omega - E_0}{\Gamma},$$

E_T is the thermal energy and $\hbar\omega_0$ the vibronic energy.

The solid lines in figures 1 and 3 are calculated to obtain the best fit with the absorption spectrum. The values of parameters for room and nitrogen temperatures are presented in table I.

Table I.

	300 K	77 K
E_0	$7\,500 \pm 25 \text{ cm}^{-1}$	$7\,525 \pm 25 \text{ cm}^{-1}$
Γ	$1\,125 \pm 25 \text{ cm}^{-1}$	$800 \pm 25 \text{ cm}^{-1}$

In the first approximation the relaxation energy $E_R = E_0 - E_T$ is taken temperature independent, and then :

$$\hbar\omega_0 = 225 \pm 10 \text{ cm}^{-1}, \quad E_R = 1\,385 \pm 25 \text{ cm}^{-1}.$$

One can deduce the thermal energy :

$$E_T = 6\,140 \pm 25 \text{ cm}^{-1}$$

at 77 K and $E_T = 6\,115 \pm 25 \text{ cm}^{-1}$ at 300 K.

The obtained values $E_0 = 0.93 \text{ eV}$ and $E_R = 0.17 \text{ eV}$ fits reasonably the values 0.97 eV and 0.16 eV found by Kocot and Kamińska [10] from photocapacity measurements. With the values of the relaxation energy $E_R = 0.17 \text{ eV}$ and the vibronic energy

$$\hbar\omega_0 = 225 \text{ cm}^{-1}$$

one can estimate in the harmonic approximation the increase of impurity — ligand distance as about 3 %.

The maximum value of the absorption cross section $\sigma_{\max}$: $\sigma_{\max} = \alpha_{\max}/N_{\text{Cr}} \simeq 5 \times 10^{-17} \text{ cm}^2$ allows to find the value of the parameter σ_0 (eq. (1)) as about 10^{-16} cm^2 . It is interesting to notice that $\sigma_{\max}$ is about one order of magnitude higher than the one found by Kamińska *et al.* [11] for $\text{Cr}^{2+} \rightarrow \text{Cr}^{1+}$ transition in II-VI semiconductors.

5. Pressure properties of the acceptor level. — Under hydrostatic pressure a small shift of the absorption spectrum was observed. The comparison of the absorption at 77 K without pressure and under the maximum pressure (9 250 bar) is shown in figure 3. The best fit of all the absorption curves (6 different pressures for each temperature) gives the linear dependence of $E_0(P)$ with the same coefficient $dE_0/dP = 2 \pm 0.3 \times 10^{-6} \text{ eV/bar}$ for both temperatures and $\Gamma(P) = \text{constant}$ within the experimental error. This pressure coefficient is very close to the value $2.1 \times 10^{-6} \text{ eV/bar}$ obtained by White *et al.* [12] from photocapacitance measurements.

6. Conclusion. — In conclusion one can state that valence band to chromium acceptor level transition is well described with the model which takes into account a totally symmetric lattice distortion around the impurity.

It is important to notice that the ground state of Cr^{3+} and Cr^{2+} are suffering a Jahn-Teller effect [6, 7], which gives an energy shift of the order of 0.05 eV, and is neglected in the present model. So the obtained parameters are a mean value of a more refined theory which should involve at least two types of distortions, a symmetric one and a non-symmetric one corresponding to the Jahn-Teller effect.

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