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CHARGE TRANSFER $Cr^{2+}(d^4) \rightarrow Cr^{1+}(d^5)$ INDUCED BY HYDROSTATIC PRESSURE IN CHROMIUM DOPED GaAs

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Hall effects measurements have been performed on n-type GaAs:Cr under hydrostatic pressure up to 11 Kbar at 77° K. These experiments evidence a trapping process of free carriers and a non linear variation of the mobility. The interpretation of the results shows that the Cr^{1+} level, degenerated with the conduction band, is the trapping center which then scatters the electron as a double acceptor state. A quantitative fit requires the assumption of a pairing between acceptor and donor impurities.

As this has been shown recently [1] , the intensity of the absorption, characteristic of the intracenter transitions of Cr^{2+} in GaAs, varies significantly under hydrostatic pressure for samples with a number n of free electrons comparable to that of the Chromium impurities N_{Cr}. If $n \lesssim N_{Cr}$, the absorption strength first decreases at 77° K between 1 bar and 10 Kbar and then saturates whereas the resistivity of the sample increases very sharply. If $n \gtrsim N_{Cr}$, the absorption strength decreases to zero in the same range of pressure, the resistivity first increases and then saturates. The interpretation of these features was involving the trapping of free carriers by the Chromium impurity Cr^{2+} (single acceptor state) and its conversion into a double acceptor state (Cr^{1+}).

The object of this work is to bring about further experimental information which support this idea. Hall effect measurements have been performed on such samples, as a function of pressure (1-12 Kbar) and temperature (77-300 K). The pressure is applied through the compression of He gas which then preserves the hydrostaticity of the medium in these thermodynamical conditions. The GaAs sample has been obtained by diffusion of Chromium on a substrate doped with Te and Si during the growth. The sample has a number of carriers of about $3.6 \times 10^{17}/cm^3$ and a mobility of 1500 $cm^2/Vsec$. at 77° K.

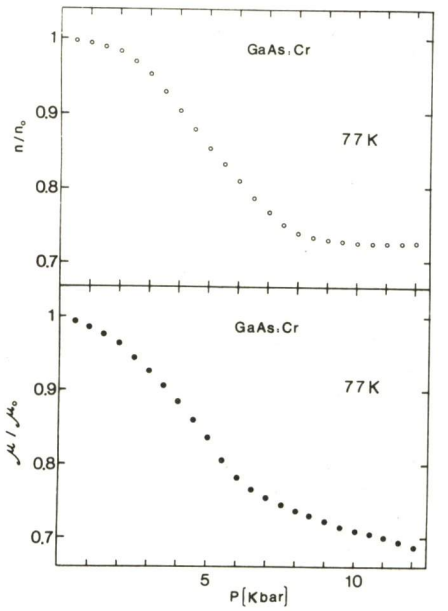

Fig.(1) Variation of the free carrier concentration $(\frac{n}{n_o})$ and of the mobility $\frac{\mu}{\mu_o}$ as a function of pressure for n-type GaAs:Cr

Fig.(1) shows the variation of the number of free carriers and that of the mobility. The variation of n shows the trapping process which is completed at around 9 Kbars. The mobility curve indicates that an additionnal scattering mechanism occurs together with the increase in the number of trapped carriers. Assuming a density of states for the trapping centers with a δ-like form (the total number of centers being N_{Cr}) the number of free carriers can be written :

$$n = n_T - \frac{N_{Cr}}{1 + g \exp \frac{E_i - E_F}{kT}} \qquad (1)$$

where n_T is the total number of free carriers, E_i is the energy of the impurity state, E_F the Fermi energy (both energies are measured from the bottom of the conduction band). The factor g entering Eq.(1) takes care of the degeneracy of the different levels and can be shown to be 5/6 in our case [2]. The value of E_F can be calculated for all pressures, since n is known. This is done, taking into account the non parabolicity of the conduction band of GaAs. The gap is assumed to vary with pressure at a rate of $\frac{\partial E_G}{\partial P} \simeq 11\times10^{-6}$ eV/bar and the different parameters entering the non parabolicity relations at 1 bar, are taken from the results of Raymond et al. [3]. From Eq.(1), E_i can be plotted as a function of pressure with two fitting parameters n_T and N_{Cr}. Since E_i should vary linearly with pressure, the fit requires a straight line as this shown in Fig.(2). This gives $n_T = 3.6\times10^{17}/cm^3$ and $N_{Cr} = 1\times10^{17}/cm^3$ E_i is found to be of 55 ± 2 meV at 1 bar and its pressure coefficient $\frac{\partial E_i}{\partial P} \simeq -6.5\times10^{-6}$ eV/bar (Both quantities are measured with respect to the bottom of the conduction band). The interpretation of the mobility results requires an additionnal scattering mechanism - Zawadzki and Szymanska [4] have shown that, at 77° K, the mobility in GaAs is still dominated by the scattering on ionized impurities. This mobility can be expressed as :

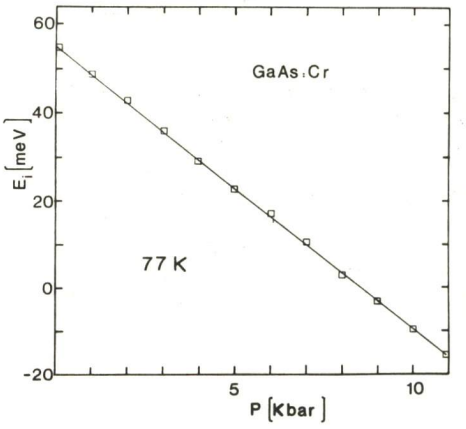

Fig.(2) Variation with pressure of the energy of the impurity level E_i with respect to the bottom of the conduction band

$$\mu = \frac{A}{Z_i^2 \, m_c^{*2}} \frac{n}{N_i} \frac{1}{F_i} \,, \qquad (2)$$

$$A = \frac{3\pi}{2} \frac{\varepsilon_o^2}{e^3} \frac{\hbar^3}{m_o^2} \,,$$

where A depends on the static dielectric constant ε_o, Z_i is the charge of the ionized center i, N_i their number, m_c^* the effective mass at the Fermi level and F_i a function of the screening length which depends also on Z_i and m_c^*. The impurities which scatter the carriers are donor impurities with a number of $8\times10^{17}/cm^3$ and the chromium impurities which can act as a single acceptor state (Cr^{2+}) or a double acceptor state (Cr^{1+}). The change of the charge of this acceptor state due to the trapping causes the non linear variation of the mobility because a double acceptor state scatters four times more efficently the electron than a single one does (Eq. (2)). The sample has also some neutral impurities which give rise to a residual mobility, the variation of which, with pressure, is assumed to be inversely proportionnal to the effective mass at the Fermi level. All the different contributions to the mobility have been calculated and compared to the experimental results.

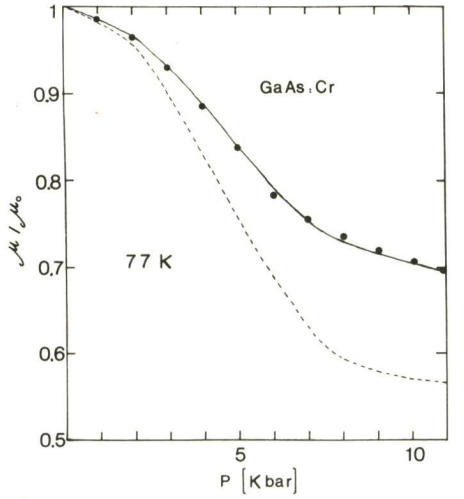

Fig.(3) Comparison between the experimental (full dots) and calculated mobility for $\alpha = 1$ (dashed line) and $\alpha = 0.5$ (full line)

The theoretical curve is drawn in Fig.(3) as a dashed line. Though the qualitative variation is reproduced, the strength of the calculated scattering process is too strong.

We then are lead to assume that a compensation occurs in the samples between donor and acceptor impurities, which in fact reduces the efficency of the scattering. A crude approach to this problem is to divide the population of Chromium impurities into two classes, a first one in which the Chromium atoms are isolated in the bulk lattice and a second one for which the Chromium atom is paired with a donor impurity. For the Coulombic scattering, this pair behaves like a neutral impurity when the Cr impurity is in the $3d^4$ configuration (Cr^{2+}) and like a single ionized acceptor when the Cr impurity is in the $3d^5$ configuration (Cr^{1+}). If we let α be the proportion of unpaired Cr impurities ($0 < \alpha < 1$), the mobility can be calculated with α as a fitting parameter. Fig.(3) shows that a quantitative agreement (full line curve) between theory and experiment is achieved with a value of about 0.5 for α. This value varies with samples of different carrier and impurity concentration [2] but remains always significantly different from 1. It is difficult to know if this result is correlated to the way of preparation of our samples which are of course highly compensated.

However we may notice that the characteristic luminescence spectrum of GaAs:Cr is the well known 0.839 eV line which has been assigned recently [5] to that of a complex of donor- Chromium pairs. So our results could evidence a pairing of Chromium with donor impurities, as a rather stable state for Chromium in GaAs.

In conclusion, this study shows that the Cr^{1+} level is degenerated with the conduction band of GaAs and that it can be activated by hydrostatic pressure.

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References

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