

# Tunneling states in GaAs:Cr

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New metastable states of a complex consisting of a Cr impurity plus a donor at an anionic site have been detected in GaAs:Cr through an optically induced modulation of the absorption. A theory is offered for this defect.

1. The variety of properties exhibited by a Cr impurity in GaAs has attracted the interest of many researchers. It has been learned that Cr in GaAs may localize in at least two distinct positions: as an isolated impurity at a Ga site having three (or even four) charge states [ $d^5$ ,  $d^4$ ,  $d^3(d^2?)$ ] and in a recently discovered bound state with a deep donor at an As site (possibly an As vacancy) in a  $\text{Cr}_{\text{Ga}}^- \text{D}_{\text{As}}^+$  configuration [ $\text{Cr}^- = \text{Cr}(d^4)$ ]. The reader is directed to Refs. 1 and 2 for a review of this question. The CrD complex has a trigonal rather than cubic symmetry, according to a study of optical transitions in the  $d$  shell of the Cr ion. In the present study we have found some new metastable states of the CrD complex with charge transfer to the donor and a long-term relaxation. We offer a qualitative microscopic theory for this complex.

2. Figure 1 shows some typical spectra of the optically induced absorption modulation at 300 K of  $p$ -type semi-insulating GaAs:Cr crystals [ $\rho \sim 10^8 \Omega \cdot \text{cm}$ ,  $\mu_x = 200\text{--}300 \text{ cm}^2/(\text{s} \cdot \text{V})$ ]. The crystals were synthesized by the Czochralski method; the melt was hermetically sealed with  $\text{B}_2\text{O}_3$  flux. The concentration of the Cr impurity was  $\sim 1.5 \times 10^{17} \text{ cm}^{-3}$ .

The method of optically induced absorption modulation is a differential method for determining the change in the absorption coefficient ( $\Delta k$ ) of a monochromatic probing beam with a photon energy  $h\nu_{\text{pr}}$  during a periodic (at frequency  $f_B$ ) charge exchange of the impurity centers by the exciting light with a photon energy  $h\nu_B$  on the order of the gap width  $E_g$  (in the case of intrinsic excitation) or  $< E_g$  (in the case of impurity excitation).<sup>3</sup> Here we have  $\Delta k(h\nu_{\text{pr}}) \geq 0$ , depending on whether the level is filled or emptied during the exchange. Temporal characteristics of the charge exchange of the levels are found from the  $\Delta k(h\nu_{\text{pr}})$  relaxation curves through repeated synchronized signal buildup.<sup>4</sup>

During the intrinsic excitation (curve 1), two broad bands are observed in the spectrum. The amplitude of the signal corresponding to the optically induced absorption modulation of the weak band,  $h\nu_{\text{pr}} < 0.9 \text{ eV}$ , does not depend on the modulation frequency ( $f_B$ ) of the exciting light, while the far more intense signal in the second band ( $> 0.9 \text{ eV}$ ) intensifies by an order of magnitude as  $f_B$  is reduced from 64 to 1.6 Hz (curve 2). The intensities of both bands follow the Cr concentration. Study of the relaxation processes at 300 K showed that the weak band has a short relaxation time  $\tau_f < 10^{-3} \text{ s}$  and  $\Delta k_f < 0$ , and the intensity falls off slowly with  $\tau_s \sim 10^{-1} \text{ s}$  and  $\Delta k > 0$ .

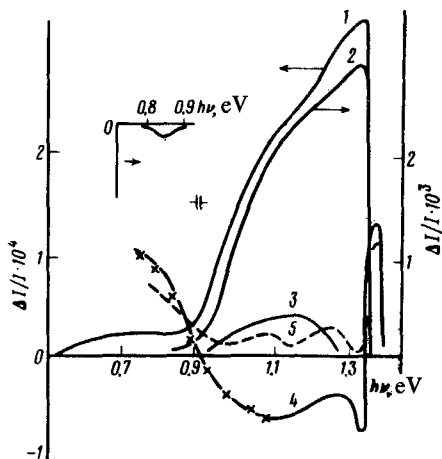


FIG. 1. 1,2,4,5—Spectra of the optically induced absorption modulation for  $h\nu_B \sim E_g$  (1,2) and  $h\nu_B < E_g$  (4,5); curve 3 and inset—absorption spectra found from the relaxation curves. 1,4,5)  $f_B = 64$  Hz; 3) 1.6 Hz.

As the temperature is lowered,  $\tau_s$  increases to the extent that it cannot be measured by the modulation method. Furthermore, the large difference between  $\tau_s$  and  $\tau_f$  made is possible to detect a resonant transition with  $h\nu_m \approx 0.85$  eV and  $\Delta k < 0$  (see the inset in Fig. 1), which corresponds to the known luminescence line at 0.839 eV which involves an intracenter in the  $\text{Cr}^-$  shell.<sup>1,2</sup>

In the spectra of the optically induced absorption modulation we measure the resultant effect of all types of differential absorption (in our case,  $\Delta k = \Delta k_s - \Delta k_f$ , where the subscripts "s" and "f" specify the slow and fast processes). During impurity excitation with  $h\nu_B < E_g$  the intensity of the slow component drops sharply (curve 3), and the values of  $\Delta k_s$  and  $\Delta k_f$  become comparable. Their spectra can accordingly be determined separately from the relaxation curves. The agreement of  $\Delta k_f(h\nu_{pr})$  with the known dependence of the absorption cross section  $\sigma_p(h\nu)$  for  $\text{Cr}_{\text{Ga}}^{3+}$  (Ref. 5; curve 4, for  $h\nu_{pr} < 1.2$  eV) means that we can attribute it to an isolated  $\text{Cr}^{3+}$  impurity (according to the rule of signs of the method of optically induced absorption modulation,  $\Delta k_{\text{Cr}^{3+}} < 0$ ). At  $h\nu_B = 1.37\text{--}1.38$  eV for  $f_B = 64$  Hz, the two contributions nearly cancel out, and it becomes possible to detect several resonant lines in the energy interval 0.9–1.33 eV with  $\Delta k < 0$  and a peak with  $h\nu_m \approx 1.38$  eV and  $\Delta k > 0$  (curve 5).

3. In constructing a model for a theoretical description of the  $[\text{CrD}]$  complex we assume for definiteness that the role of the donor is played by an anionic vacancy  $V_{\text{As}}$ . According to this model, both  $\text{Cr}_{\text{Ga}}$  and  $V_{\text{As}}$  create deep levels of  $t_2$  symmetry in the energy gap; the  $\text{Cr}^-$  level (which is not filled in its ground state) lies below the filled  $V^0$  level (Fig. 2a). As  $\text{Cr}_{\text{Ga}}$  and  $V_{\text{As}}$  close on each other, there can thus be a transfer of an electron from the vacancy,  $\text{Cr}^0(d^3) + V^0 \rightarrow [\text{Cr}^-V^+]$ , resulting in the formation of a complex of trigonal symmetry. Because of the pronounced localization of the wave function near each of the defects making up the complex, the electron has an asymmetric two-well potential (see the inset in Fig. 2a), and in the limit  $T \rightarrow 0$  its transfer occurs by tunneling.

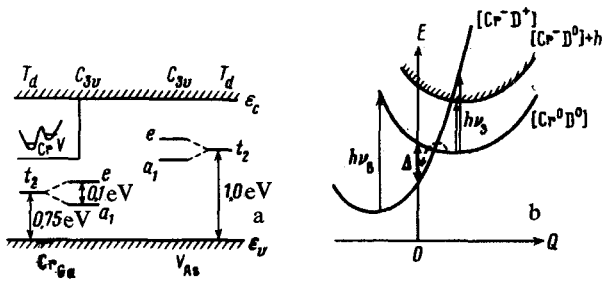


FIG. 2. a— $\text{Cr}_{\text{Ga}}$  and  $\text{V}_{\text{As}}$  levels in the tetrahedral ( $T_d$ ) and trigonal ( $C_{3v}$ ) fields (1,6) (the inset shows the potential relief for the  $t'_2$  electron); b—configuration diagram for the ground and excited states of the  $[\text{CrD}]$  complex. The arrows show optical transitions caused by the exciting light ( $h\nu_{pr}$ ) for slow processes, while the dashed arrow shows a transition corresponding to the long-term relaxation of the spectra of the optically induced absorption modulation.

The Hamiltonian of the system is

$$H = -\nabla^2/2m + U(r) - U_{\text{As}}(r - R_{\text{V}}) + U_d(r - R_d) - U_{\text{Ga}}(r - R_d) + V_1 \{ \Delta\rho(r) \}, \quad (1)$$

where  $U$  is the potential of an ideal lattice;  $U_{\text{As}}$ ,  $U_{\text{Ga}}$ , and  $U_d$  are the potential of the anion, cation, and the  $d$  impurity;  $\Delta\rho$  is the perturbation caused in the valence-electron density by the defect; and  $V_1$  is the corresponding potential. The potential  $U_d$  is a resonant potential, by which we mean that it contains the intrinsic level of the  $d$  electron,  $E_d$ . Assuming the resonant scattering to be dominant, we find an equation for the Green's functions of Hamiltonian (1) (cf. Ref. 7):

$$G_i(r, r') \doteq G_{i0}(r, r') + \int G_{i0}(r, r_1) U'_i(r_1) G_{j0}(r_1, r_2) U'_j(r_2) G_i(r_2, r') dr_1 dr_2, \quad (2)$$

$$(i = v, d),$$

where the  $G_{v,d}$  are the Green's functions of an electron in a semiconductor with a vacancy and with a  $d$  electron, respectively, the subscript 0 specifies an isolated defect, and the  $U'_{v,d}$  are the trigonal perturbations of these defects, found from (1). The function  $G_{v0}$  has a pole  $E_v$  in the gap which corresponds to a vacancy level, in addition to the states of a continuum with a density  $S(E)$ :

$$G_{v0}(r, r') = \int \frac{dES(E) |E\rangle \langle E|}{\omega - E} + \frac{|v\rangle \langle v|}{\omega - E_v}. \quad (3)$$

This function has been found through numerical calculations<sup>6</sup> for the  $\text{GaAs}:\text{V}_{\text{As}}$  system. The discrete poles of the Green's function  $G_i$  are determined by the equation

$$\prod_{\tau} (\omega - \tilde{E}_{d\tau}) = g^2 \sum_{\tau} (\omega - \tilde{E}_{d\tau}) \sum_{\tau'} (\omega - E_{v\tau'})^{-1}, \quad \tilde{E}_{d\tau} = E_{d\tau} + \int \frac{dES(E) |E\rangle \langle U'| d\tau|^2}{\omega - E}. \quad (4)$$

Here  $E_{d\tau}$  and  $E_{v\tau}$  are the initial levels of the impurity and the vacancy, which are split by the trigonal fields  $C_{3v}$ ;  $\tau = a_{1,e}$  (Fig. 2a); and  $g = \langle d\tau | U'_d | v\tau \rangle$  is the integral representing the tunneling between the two wells.

The wave function of an electron bound with the complex is

$$\psi(r, R_d, R_v) = \sum_{\tau} a_{\tau}(\omega) \psi_{d\tau}(r - R_d) + \sum_{\tau'} b_{\tau'}(\omega) \psi_{v\tau'}(r - R_v) + \int dE C_{\tau}(E) S(E) \psi_E(r). \quad (5)$$

Ignoring the splitting and the contribution of the continuum, we find from (2) and (4)

$$a^2(\omega) \cong g^2 [(E_d - \omega)^2 + g^2]^{-1}, \quad b^2(\omega) \approx 1 - a^2(\omega), \quad (6)$$

$$\omega = \omega_{1,2} \approx \frac{1}{2} \{ [E_v + \tilde{E}_d] \mp [(E_v - \tilde{E}_d)^2 + 4g^2]^{1/2} \}.$$

Under the conditions  $E_v - E_d > 0$  and  $g^2/(E_v - E_d)^2 \equiv \beta \ll 1$  we find  $d^2 \approx 1 - 0(\beta)$ , so that in the  $\omega_1$  ground state the electron density is displaced toward the impurity site; i.e., the state is near  $[\text{Cr}^- \text{V}^+]$ , and the excitation of the center to the  $\omega_2$  level is accompanied by a significant charge transfer,  $[\text{Cr}^- \text{V}^+] \rightarrow [\text{Cr}^0 \text{V}^0]$ , and a pronounced lattice relaxation. Responsible for this relaxation is the local mode  $Q$  of symmetry<sup>8</sup>  $T_2$ , which corresponds to a displacement of the  $\text{Cr}_{\text{Ga}}$  ion along the  $\langle 111 \rangle$  axis toward the As. The relaxation is described by the Hamiltonian

$$H_Q = k_{\omega} Q^2/2 + W_{\omega} Q, \quad W_{\omega_{1,2}} = d\omega_{1,2} / dQ |_{Q=0}. \quad (7)$$

In the approximation  $\beta \ll 1$  the constants of the vibron interaction are

$$W_{\omega_1} \approx -(1 - \beta^2) dY/dQ |_{Q=0} - 2\beta dg/dQ |_{Q=0} (1 - Y/\Delta), \quad (8)$$

$$W_{\omega_2} \approx -\beta^2 dY/dQ |_{Q=0} + 2\beta dg/dQ |_{Q=0} (1 - Y/\Delta), \quad \Delta = (E_v - E_d) |_{Q=0}.$$

Here the integral  $Y$  represents the intersite Coulomb interaction, which dominates the renormalization  $E_i \rightarrow E_{i\tau}$  in (4):

$$Y = \epsilon^{-1} \int |\psi_d(r)|^2 |\psi_v(r')|^2 (|r - r' + R_0 + Q|)^{-1} dr dr', \quad dg/dQ < 0, \quad dY/dQ < 0. \quad (9)$$

The increment caused in the elastic constant  $k_{\omega}$  of the bond stretching by the additional Coulomb stretching is important only at  $\omega = \omega_1$ :

$$k_{\omega_1} \approx k_0 + d^2 Y/dQ^2, \quad k_{\omega_2} \approx k_0 - 0(\beta). \quad (10)$$

By virtue of (8)–(10), the equilibrium positions of the defect in the states  $\omega_1$  and  $\omega_2$  are displaced in opposite directions from the value  $R_0 = |R_d - R_v|$  for the noninteracting defects, and the frequencies of the local vibrations are different. Figure 2b shows a configuration diagram for  $H_Q$  in (7).

4. The processes with long relaxation times detected in the spectra of the optically induced absorption modulation can be interpreted with the help of the diagrams in Fig. 2b. Band (1,2) in Fig. 1 with  $\Delta k < 0$  and a long-term relaxation ( $h\nu_{\text{pr}} > 0.9$  eV) corresponds to ionization of the  $[\text{Cr}^0 \text{D}^0]$  metastable state which is created by the exciting light  $h\nu_B$ . On the edge of this band we see a comparatively narrow peak with  $h\nu_m \approx 1.33$  eV, which can be attributed to a transition of the defect back to the  $[\text{Cr}^- \text{D}^+]$  state, but to a configuration far from equilibrium. The relaxation time  $\tau_s \sim 10^{-1}$  s is governed primarily by the inverse charge exchange of the  $[\text{Cr}^0 \text{D}^0]$  metas-

table state. Its temperature dependence at  $T > 300$  K has an activation energy with a barrier  $\sim 0.2$  eV. The trigonal splitting of the  $\omega_{1,2}$  levels due to the  $E_i \rightarrow E_{it}$  renormalization, which can be found from (4), explains the fine structure of the spectra of the optically induced absorption modulation (curve 5 in Fig. 1). Finally, the peak with  $\Delta k > 0$  at 1.38 eV can be attributed to either the excitation of a "donor" exciton,<sup>9</sup> [ $\text{Cr}^0\text{D}^+e$ ], or a modulation of the absorption edge by the intrinsic field of the impurities as a result of their optical charge exchange (an internal Franz-Keldysh effect).<sup>10</sup>

Tunneling states of this type should arise in "binary" defects in all cases in which each component of the complex has deep intrinsic levels. In particular, it may be suggested that the long-term relaxation in the GaP:Fe system<sup>11</sup> is also due to a pseudo-Jahn-Teller restructuring of the lattice upon the charge exchange of a binary center.

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