Stark effect in shallow donors in gallium phosphide

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The Stark effect has been observed for the first time for hydrogen-like impurity centers in a semiconductor. Electron transitions, forbidden in the absence of an electric field, were discovered between the components of the 1*S* state, split by a valley-orbital interaction.

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This paper presents the results of a study of the Stark effect in donor centers in gallium phosphide. The choice of this material as the subject of study is based on the following important circumstance: when singly charged donors retain a hydrogen-like character in GaP, their ionization energy amounts to $E_d \approx 100$ meV. This is considerably higher than in germanium and silicon and makes it possible to create in a doped GaP specimen static electric fields at a level of $\mathscr{E} \sim 10^6$ V/m even at a temperature of ~ 20 K. For germanium and silicon this is achieved only at temperatures of ~ 3 and 10 K, respectively. This probably explains why there are no data in the literature on the Stark effect in shallow impurity levels in these materials.

We have investigated the modulation electroabsorption (EA) spectra of *n*-GaP single crystals. The samples were cut from ingots, grown by the Czochralski method and doped with sulfur, tellurium or silicon to a level of 5×10^{17} cm^{-3}. The procedure for creating an electric field in the sample was similar to that in Ref. 1. The measurements were made in the 5–25 μm spectral region using a vacuum cryostat and an IKS-14 monochromator.

Examples of the EA spectra, obtained on GaP:S samples, are shown in Fig. 1a and Fig. 2. Simple features are clearly visible in the spectra at phonon energies $\hbar\omega$ of about 54 and 71.5 meV and there is a complicated structure visible in the 80–110 meV region, the most characteristic element of which is a negative peak near 97 meV. The optical absorption lines located at 71.5 and 97 meV were previously identified in the

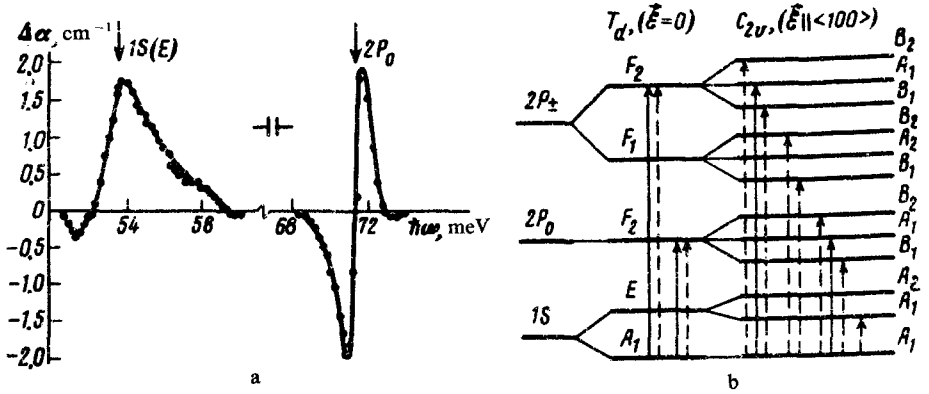

FIG. 1. a—Features of GaP:S EA spectrum in the 50–80 meV photon energy region. $T \approx 20$ K, $\mathscr{E} = 0.6 \times 10^6$ V/m. The spectral dependence of the change $\Delta\alpha$ in the absorption coefficient in an electric field is plotted. The electric field intensity vector $\vec{\mathscr{E}}$ and the photon wave vector $\mathbf{k}_{\text{phot}}$ are mutually perpendicular and are directed along ⟨100⟩. The arrows indicate the expected locations of the features.[2-4] b—Splitting scheme of energy levels of group VI donor center in GaP in an electric field. The notations of the irreducible representations correspond to those in Ref. 5. The arrows indicate the optical transitions allowed in the dipole approximation: solid line-radiation polarization vector $\mathbf{e} \| \vec{\mathscr{E}}$; dashed line-$\mathbf{e} \perp \vec{\mathscr{E}}$.

photoexcitation spectra of GaP:S[3,4] and were ascribed to the $1S\,(A_1) \rightarrow 2P_0$ and $1S\,(A_1) \rightarrow 2P_\pm$ transitions, respectively (see scheme in Fig. 1b). The relatively weak negative maxima at photon energies of 112, 126 and 144 meV correspond to phonon repititions of the $2P_\pm$ line.[6] The lines at $\hbar\omega = 54$ meV did not appear in the photoexcitation spectra.

The form of the 71.5-meV feature in the EA spectrum (Fig. 1a) indicates a shift of the components of the $2P_0$ level, split in the electric field.

In contrast to this, for the 54-meV feature the integral change $\Delta\alpha(\hbar\omega)$ is significantly positive. This behavior is characteristic of transitions that are forbidden at $\mathscr{E} = 0$. In this region of the spectrum, as seen from Fig. 1b, one can observe only the $1S\,(A_1) \rightarrow 1S\,(E)$ transition between the components of the $1S$ state, split by a valley-orbital interaction. Then, we obtain $\Delta = 1S\,(E) - 1S\,(A_1) = 54.0 \pm 0.5$ meV for the magnitude of this splitting, which agrees well with the value $\Delta = 53.4$ meV, previously obtained from Raman scattering spectra[2] and which had not been verified.

The typical form of the spectrum in the 80–110 meV region (negative peak, bounded by positive wings) can be observed in two cases: either with the broadening of the optical absorption line in an electric field or in the presence of splitting with a shift of the components in opposite directions, simulating broadening. In order for the observed spectral shape to be explained by a broadening of the $2P_\pm$ line, it is necessary to assume that the broadening has an anomalously large value of $\Delta\Gamma \approx 0.2$ meV and exceeds the theoretical estimate of $\Delta\Gamma\, 3 \times 10^{-3}$ meV by more than an order of magnitude (for $\mathscr{E} = 2 \times 10^5$ V/m). In addition, in this case it is necessary to explain

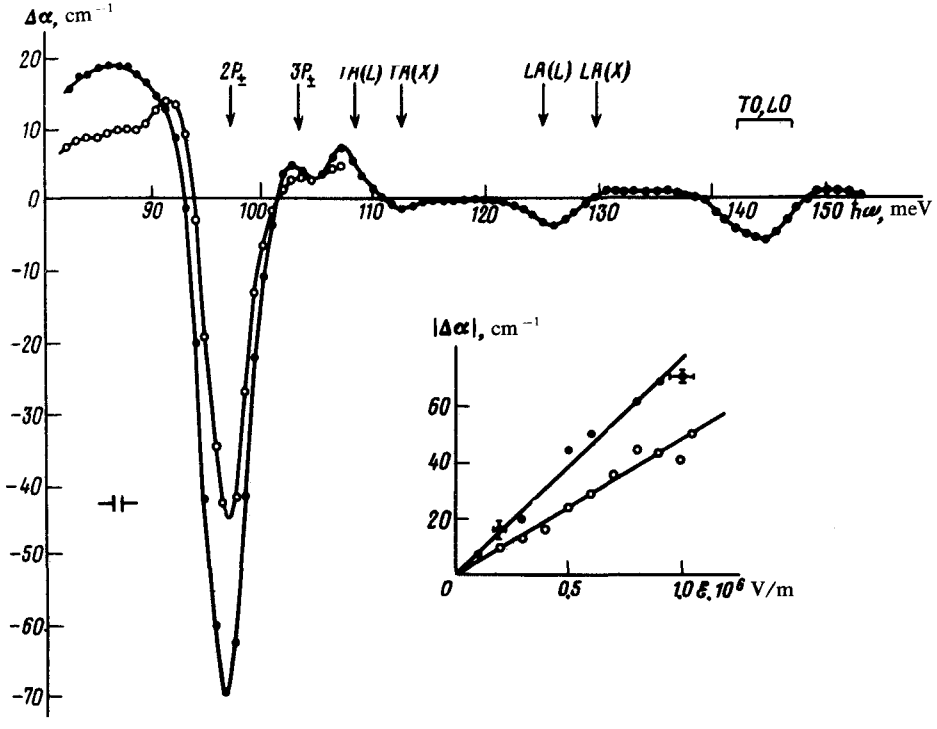

FIG. 2. EA spectrum of GaP:S in 80–160 meV photon energy region. $T \approx 20$ K, $\mathscr{E} = 0.9 \times 10^6$ V/m. Orientation of $\vec{\mathscr{E}}$ and $\mathbf{k}_{\text{phot}}$ is the same as that given in Fig. 1a. Dark circles-e$\|\vec{\mathscr{E}}$, open circles-e$\perp\vec{\mathscr{E}}$ (data are given for only the 80–110 meV region). Arrows indicate location of line and the features in GaP:S photoexcitation spectrum.[3,4,6] Inset shows the dependence $\Delta\alpha(\vec{\mathscr{E}})$ for the maximum of the negative peak ($\hbar\omega = 96.5$ meV).

the strong dependence of the spectral shape on the direction of polarization (Fig. 2). In particular, the location of the negative peak for different polarization directions differs by an amount of ~0.5 meV. The splitting of the $2P_{\pm}$ level should be linear in nature since the symmetry group of the substitution donor center in GaP (group T_d) has no inversion center. This is experimentally confirmed by the linear dependence of the EA signal on the electric field intensity, as seen in the inset of Fig. 2.

Thus, the structure of the EA spectrum in the region of the $2P_{\pm}$ photoexcitation line is determined by the linear Stark splitting of the $2P_{\pm}$ level of the donor center. As seen in Fig. 1b, in an electric field, parallel to the ⟨100⟩ direction, this level is split into six components of different symmetry. In addition, because of the presence of the "two-hump" structure of the X_{1C} minimum of the GaP conduction band[3] the excited $3D_{\pm}$ state of the donor, as shown by the theoretical calculation that has been made, lies only 0.5–1.0 meV above the $2P_{\pm}$ state.[1)] For $\mathscr{E} \neq 0$ the $3D_{\pm}$ state, having $F_1 + F_2$ symmetry, should be highly intermingled with the $2P_{\pm}$ state; therefore, a detailed interpretation of the structure of the EA spectrum in the vicinity of the $2P_{\pm}$ line is a laborious problem.

The data we have obtained in studies of the EA spectra when Te and Si donors take part completely agree with the data presented for the GaP:S case.

[1)]The dispersion law of an electron near the X_{1C} minimum of the GaP conduction band has a "two-hump" structure, with the two adjacent minima being separated by an energy "hump" of only 3.5 ± 0.3 meV in size.[3,7] It is obvious that the excited states of donors with a binding energy of this order of magnitude will be grouped in pairs (even and odd), analogously to the so-called inversion doubling.

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