Symmetry and metastability of an EL2 center in GaAs

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The symmetry and mechanisms of metastability of the EL2 center in GaAs were identified using data obtained by the methods of photo-ESR, piezospectroscopy, and Stark spectroscopy. The results obtained demonstrate clearly the C_{3v} symmetry of the investigated antisite double donor, whose charge states [$D^+ = As_{Ga}^+$, $D^0 = (As_i V_{Ga})^0$ and $D^{++} = (As_i V_{Ga})^{++}$] correspond to positions at a site, and in tetrahedral and hexagonal interstices of the GaAs lattice. These states are formed from, respectively, the wave functions of the Γ, L, and X valleys of the conduction band. The transition of the EL2 center to a metastable state is a consequence of a charge exchange process of the $2D^{++} + h\nu \rightarrow D^0 + D^{++}$ type, which initiates tunneling of the As_{Ga} antisite defect from a lattice site to a tetrahedral interstice. The temperature and rate of annealing of the metastable neutral state of the EL2 center are governed by the height of an energy barrier opposing the $D^0 + h \rightarrow D^+$ reaction.

1. INTRODUCTION

The deep double donor EL2 in GaAs ($D^0/D^+ \rightarrow E_c - 0.75$ eV is the level of EL2, and $D^+/D^{++} \rightarrow E_v + 0.52$ eV) is a constant object of various investigations because its presence in single crystals and epitaxial films simultaneously ensures high carrier mobility and semiinsulating properties.[1] The basis of the EL2 center is an antisite double donor As_{Ga}, which is manifested by total correlation of the spectral dependences of the metastable quenching of the photocapacitance, photoconductivity, and of the corresponding ESR spectrum in the case of semi-insulating GaAs, as manifested in Refs. 1–4. Such quenching appears as a result of a reduction in the photocarrier lifetime when a sample is illuminated with light of $h\nu = 1.0$–1.3 eV energy, which can be explained in particular by a mechanism which transfers a neutral antisite donor to a tetrahedral interstice: $As_{Ga}^0 + h\nu \rightarrow (As_i V_{Ga})^0$ (Refs. 5 and 6). The excited state of the EL2 center $(As_i V_{Ga})^0$ is metastable for $T < 140$ K, so that regeneration of the properties of material is not observed when the pump light is switched off.[1–3]

Another characteristic feature of the EL2 center in GaAs is the occurrence of three singularities in the spectral dependence of the absorption coefficient ($E = 0.8$, 1.0, and 1.3 eV), which had been identified by photocapacitance spectroscopy as due to optical electronic transitions between the EL2 level and the Γ, L, and X conduction-band valleys, respectively.[1,2] However, these singularities have been attributed more recently to intracenter transitions in the system of the EL2 center because the zero-phonon line ($E = 1.039$ eV) observed in the absorption spectra does not appear—in the first approximation—in the relevant spectral dependence of the photocurrent,[7] and the disappearance of the zero-phonon line as a result of preliminary pumping with light of energy $h\nu = 1.0$–1.3 eV is external evidence of the intracenter nature of the optical transitions responsible for the transformation of the EL2 center to a metastable state.[7–9]

The symmetry of the EL2 center was first determined in an investigation of the characteristics of the splitting of the zero-phonon line (1.039 eV) when GaAs:EL2 single crystals were subjected to uniaxial compression.[9] These results were interpreted using a model of an isolated As_{Ga} defect with T_d symmetry,[9] which is in conflict with the later ESR, ENDOR, and piezocapacitance spectroscopy data, according to which the EL2 center is a complex with C_{3v} symmetry: $As_{Ga} + As_i$ (Refs. 10–12).

Therefore, the problem of identification of the mechanism of the metastability and symmetry of the EL2 center in GaAs remains unsolved. This is particularly true of the determination of the relative contributions of the intracenter and interband transitions to the metastable quenching process described above, especially as the zero-phonon line (at 1.039 eV) still appears—according to the latest data[13]—in the spectral dependence of the photocurrent. Moreover, the coincidence of the quenching spectra of the ESR and photocapacitance of GaAs:EL2 is in general paradoxical in relation to accepted models of the EL2 center,[1,2,5,6,9–11] since the ESR quenching process is due to a reduction in the concentration of the paramagnetic As_{Ga}^+ centers,[3,10] whereas the photocapacitance quenching is explained by a transition to the metastable state of the As_{Ga}^0 center.[1,2,5,6] It is therefore not clear whether there are two neutral states for an antisite donor in GaAs: the ground state at the lattice site and the excited state at a tetrahedral interstice, or whether the results can be explained by postulating that the neutral state of the EL2 center always has the C_{3v} symmetry. In the latter case the metastability of the EL2 center should be due not to the intracenter transitions, but due to $As_{Ga}^+ \rightarrow (As_i V_{Ga})^0$ charge transfer processes, which stimulate tunneling of a defect from a lattice site to a tetrahedral interstice.

We shall identify the appropriate model of the EL2 center on the basis of the data from a comprehensive investigation of the anisotropy of the influence of an electric field on the photocapacitance quenching processes, and also on the basis of optical absorption under conditions of hydrostatic and uniaxial compression of GaAs single crystals. We shall demonstrate a relationship between the metastable states and the symmetry of various charge states of a deep defect, on the one hand, and the structure of the conduction band, on the other.

2. EXPERIMENTS

Piezospectroscopic investigations of the optical transmission of n-type GaAs samples [$n(77\ \text{K}) = 1.5 \times 10^{16}$ cm^{-3}] grown by the Bridgman method were carried out at

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$T = 4.2$ K under hydrostatic and uniaxial compression conditions. In the uniaxial compression case we used GaAs single crystals ($3\times3.5\times7$ mm) the longest side of which was oriented along one of the crystallographic axes [111], [100], or [110], and was the direction of compression. The measurements were carried out using parallel and perpendicular polarizations of light relative to the direction of uniaxial compression. It should be pointed out that in the course of piezospectroscopic investigations the intensity of monochromatic light was maintained at a low level in order to avoid transformation of the EL2 center to its metastable state.

The transition to the EL2 metastable state was investigated, on the other hand, at a high pump light intensity ($h\nu = 1.0$–1.3 eV), so as to induce quenching of the capacitance, of the zero-phonon line (1.039 eV) in the optical absorption spectrum, and of the corresponding ESR spectrum. Special attention was paid to analyzing the spectral dependence of the quenching and regeneration of the characteristics of the EL2 center, and to identifying the role of its components (double antisite donor and interstitial arsenic) in the recombination of nonequilibrium carriers in GaAs with different types of conduction. With this in mind we investigated the quenching kinetics of the zero-phonon line (1.039 eV) as a function of the position of the Fermi level in GaAs samples with different degrees of compensation of the EL2 centers.

In addition to an investigation of the mechanism of the metastability of the EL2 center, we used the photocapacitance method to determine the symmetry of this center. It should be pointed out that in its standard form the capacitance spectroscopy method can provide information only on the energy characteristics of a point center and is unsuitable in practice for the identification of the position of such a center in the crystal lattice. However, the latter task can be successfully performed by the piezospectroscopic and Stark variants, which make it possible to investigate the behavior of the capacitance signal as a function of the direction of uniaxial pressure[12] and of an electric field[14] relative to the crystallographic axes of a GaAs:EL2 single crystal. Therefore, we investigated the relationship between the metastable properties and symmetry of the EL2 center by employing a photocapacitance analog of the Stark spectroscopy method. The Schottky diodes investigated were formed by depositing gold on a face perpendicular to the length of a single crystal grown by the Czochralski method (Cz–GaAs, dimensions $1.3\times1.5\times7$ mm) oriented along one of the crystallographic axes [111], [100], [110], or [$\bar{1}1\bar{1}$]. This ensured that the electric field in the Schottky diode was oriented exactly along a selected crystallographic direction. The homogeneity of the distribution of the free-electron density, whose value was $(1.0$–$1.5)\times10^{16}$ cm^{-3}, created by the initial tellurium impurity, was monitored using the capacitance-voltage characteristics. The metastable quenching of the photocapacitance signal was detected in various electric fields during illumination of samples with monochromatic light. These kinetic dependences were used to find the photocapacitance quenching spectra of Cz–GaAs:EL2 for different orientations of the electric field relative to the crystallographic axes.

3. RESULTS AND DISCUSSION

Piezospectroscopy of the EL2 center in GaAs

In the course of our investigation we obtained the optical absorption spectra (Figs. 1a and 1b), a study of which made it possible to determine changes in the energy positions of the zero-phonon line (1.039 eV) and of the optical transition of the EL2 center to a metastable state (1.18 eV), as a function of the hydrostatic pressure (Fig. 1c). Clearly, an increase in this pressure reduced the energy E_1 of the optimal transition to the metastable state (its value was within the interval 1.0–1.3 eV), whereas the zero-phonon line E_2 shifted toward higher energies. The frequency of the phonon replicas (11 meV) remained unchanged. These results were in good agreement with the data reported in Ref. 15 and they demonstrated that the investigated optical transitions (E_1 and E_2) were induced by different charge states of the EL2 center in GaAs. The shifts ΔE_1 and ΔE_2 were fully correlated with the corresponding changes in the energy gaps between the conduction-band valleys of GaAs (Ref. 16), as shown in Fig. 1c: $\Delta E_1 = \Delta_{X\Gamma}(p)$ and $\Delta E_2 = -\Delta_{L\Gamma}(p)$.

This interrelationship between the optical transitions and the structure of the conduction band can be explained by a model of a deep center with nonmonotonic dependence of the electron–phonon interaction constant on the charge and spin states[17,18] (Fig. 2). In this case a deep-level defect represents a tunnel system in which the lattice positions of the various charge states are characterized by different symmetries and belong to different conduction band valleys. In the case of the EL2 center in GaAs the D^+ state occupies a position at a lattice site and is formed from the wave functions of the Γ conduction-band valley, whereas D^0 and D^{++} are the states in the tetrahedral and hexagonal interstices and are associated with the L and X valleys, respectively (Figs. 2 and 3). In other words, the state $D^0 = (\mathrm{As}_i\mathrm{V}_{\mathrm{Ga}})^0$ has the C_{3v} symmetry and the EL2 level is formed from the wave functions of the L valley. At first sight, the D^+ and D^{++} states should have the T_d and D_{2d} symmetry, respectively. However, the symmetry of D^+ is lowered to C_{3v} because of reconstruction of the nearest arsenic site ($\mathrm{As}_i\mathrm{V}_{\mathrm{As}}$), as shown in Fig. 3, which affects also the ENDOR data that have been used to identify the EL2 center as the complex $\mathrm{As}_{\mathrm{Ga}} + \mathrm{As}_i$ (Ref. 11). The symmetry of the D^{++} state also

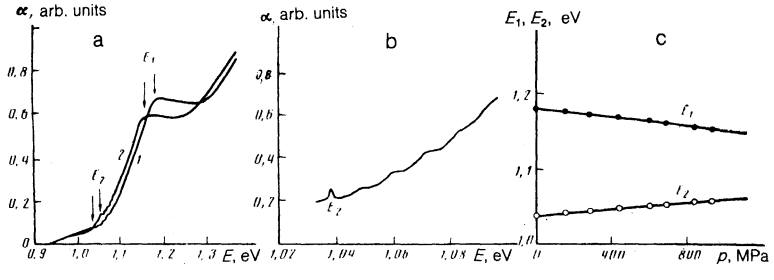

FIG. 1. a) Optical absorption spectrum of GaAs:EL2: 1) $p = 0$; 2) $p = 950$ MPa; the arrows identify the positions of an optical transition to a metastable state (E_1) and of the zero-phonon line (E_2). b) Fragment of an optical absorption spectrum with the zero-phonon line (E_2): $p = 0$. c) Dependence of the energies E_1 and E_2 on the hydrostatic pressure. The continuous curves are calculated on the basis of Ref. 16.

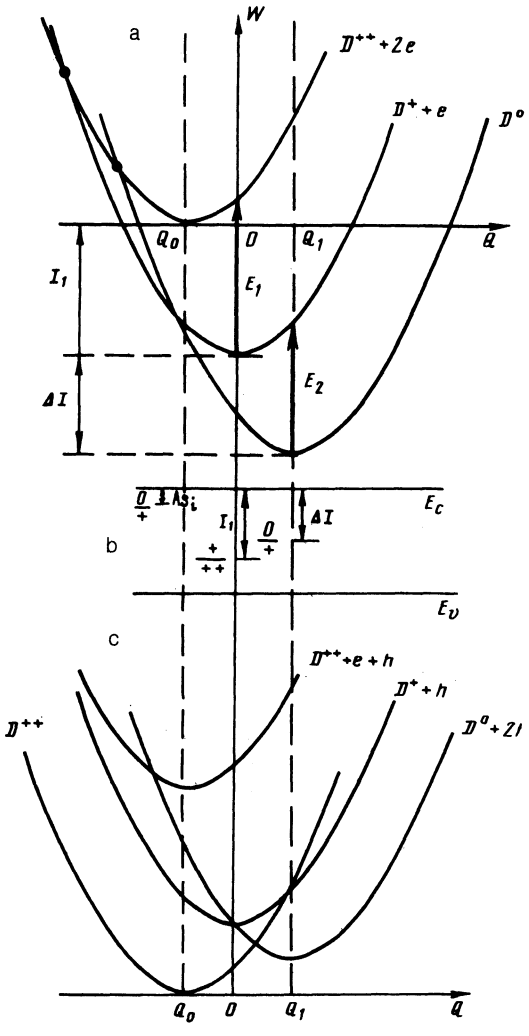

FIG. 2. Adiabatic potentials (a, c) of different charge states of the EL2 center in GaAs in the case of defect–conduction band (a) and valence band–defect (c) optical transitions; $I_2 = I_1 + \Delta I$. b) Equivalent energy band scheme; $Q \| [111]$.

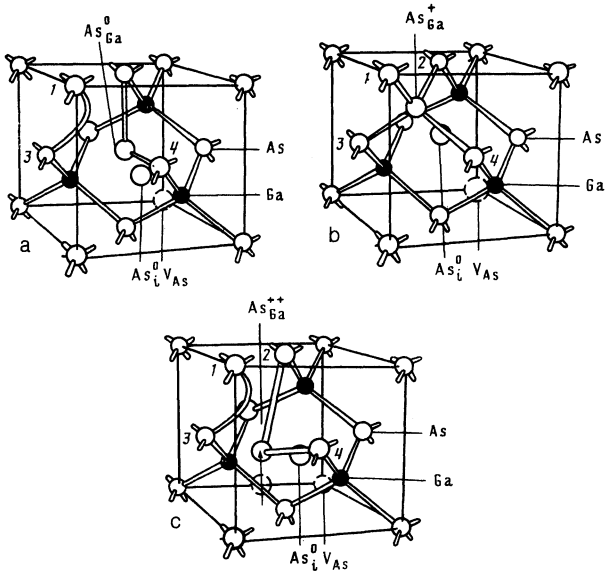

FIG. 3. Model of the EL2 center in GaAs: a) D^0 state; b) D^+ state; c) D^{++} state.

tends to C_{3v} (Fig. 3), but is due to the Stark effect which induces compensating acceptors.[17]

It therefore follows that the $D^0 \rightarrow D^+$ optical transition, whose optimum corresponds to the zero-phonon line (Fig. 2a), is accompanied by tunneling of the EL2 center from the tetrahedral interstice to the lattice site, which results in intervalley scattering of electrons $[\Delta E_2 = -\Delta_{L\Gamma}(p)]$, photoexcited from the EL2 level to the L valley of the conduction band. This is manifested most strikingly under the conditions of hydrostatic compression of GaAs single crystals (Fig. 1c). Similar intervalley scattering is experienced by an electron photoexcited to the Γ conduction-band valley as a result of the D^+/D^{++} transition $[\Delta E_1 = \Delta_{X\Gamma}(p)]$.

The structure of the conduction band also affects the processes of optical absorption in a GaAs crystal with the EL2 centers subjected to uniaxial compression (Fig. 4). The strongest splitting of the zero-phonon line was observed under the compression σ along the [111] axis. Compression of a single crystal along [100] did not split the zero-phonon line E_2, whereas in the $\sigma \| [110]$ case, it had three components whose behavior demonstrated the occurrence of the dynamic Jahn–Teller effect. It should be pointed out that the direction of compression should ideally correspond to the selected crystallographic axis, for example [100] (Fig. 4b). In the opposite case we can expect an admixture of the compression along [111], which must undoubtedly result in slight splitting of the zero-phonon line, as was indeed observed earlier.[9]

The characteristics of the induced splitting of the spectral lines corresponding to allowed transitions in a system of centers of different symmetry in cubic crystals were calculated by Kaplyanskiĭ.[19] The following main criteria govern the splitting: the intensity, the degree of polarization, and the number of the split components, as well as their shifts from the undisplaced spectral line position. Using the results of Ref. 19 and those reported above (Fig. 4), we reach an unambiguous conclusion that the symmetry of the EL2 center in GaAs is C_{3v}. The full pattern of the splittings of the zero-phonon line is in good agreement with the results of studying the way the uniaxial pressure affected splitting of the L conduction-band valley, observed in a study of the hot photoluminescence in GaAs reported in Ref. 20. In particular, the shift of the zero-phonon line in the $\sigma \| [100]$ case (Fig. 4b)

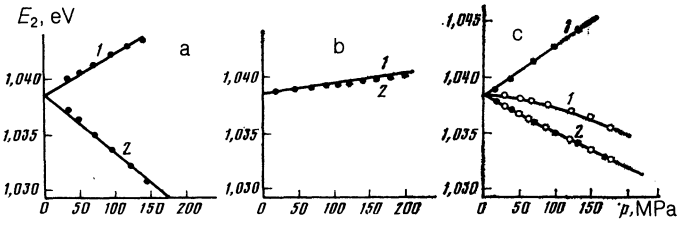

FIG. 4. Dependence of the zero-phonon line energy on the uniaxial pressure $\sigma \| [111]$ (a), $\sigma \| [100]$ (b), and $\sigma \| [110]$ (c), obtained for different polarizations of light: 1) $\mathbf{E} \perp \sigma$; 2) $\mathbf{E} \| \sigma$. The continuous line in Fig. 4b is the pressure dependence $|(1/3)\Delta_{L\Gamma}(p)|$ based on the data of Ref. 20. The black dots in Fig. 4c represent the Poynting vector $\mathbf{S} \| [\bar{1}10]$ and the open circles correspond to $\mathbf{S} \| [00\bar{1}]$.

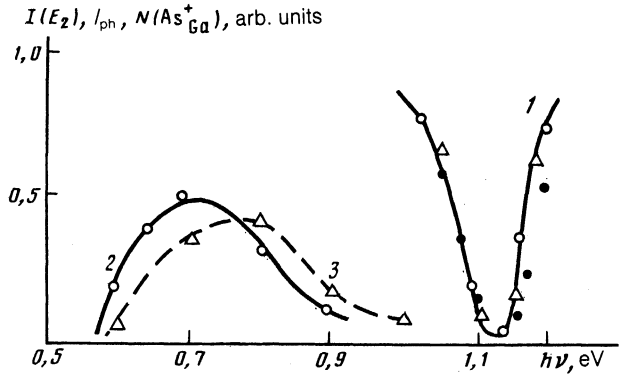

FIG. 5. Spectra of GaAs:EL2: 1) quenching of the zero-phonon line at $E_2 = 1.039$ eV (●), of the interband photoconductivity (○), and of the ESR of the As^+_{Ga} centers (△); 2) subsequent regeneration of the interband photoconductivity; 3) ESR of As^+_{Ga} centers.

corresponds to the intervalley splitting: $\Delta E = -(1/3)\Delta_{L\Gamma}$. This also provides an independent confirmation that the EL2 level belongs to the L conduction-band valley and accounts also for the presence of the zero-phonon line in the spectral dependence of the photocurrent.[13]

Therefore, an investigation of the optical absorption under the conditions of hydrostatic and uniaxial compression of GaAs single crystals demonstrated that the D^0, D^+, and D^{++} states of the EL2 center have C_{3v} symmetry and are formed from the wave functions of the L, Γ, and X conduction-band valleys, respectively.

Quenching and regeneration of the ESR spectrum of the EL2$^+$ centers in GaAs

In the course of prolonged strong pumping with light of the $h\nu = E_1$ energy the two-electron capture processes begin to dominate,[17] which induces transformation to a metastable state of the residual concentration of singly charged EL2 centers (Fig. 2a):

$$\left.\begin{array}{l} D^+ + h\nu(E_1) \to D^{++} + e, \\ D^{++} + 2e \to D^0, \end{array}\right\} \; 2D^+ + h\nu(E_1) \to D^0 + D^{++}. \qquad (1)$$

These processes represent an optical analog of the negative-U reaction[17,18,21] and account for the quenching of the ESR of the EL2$^+$ centers in the region where $h\nu = 1.0$–1.3 eV (Fig. 5), accompanied by a corresponding increase in the concentration of the EL2^0 centers. However, optical pumping using light with $h\nu = E_1$ energy induces not an increase in the intensity, but quenching of the E_2 zero-phonon line (Figs. 5 and 6) and of the photocapacitance (Figs. 7 and 8), which are at first sight proportional to the concentration of the EL2^0 centers. As pointed out above, this paradoxical situation is due to a steep reduction in the nonequilibrium carrier lifetime because of strong Auger recombination in the course of filling of the EL2 centers with electrons [$\mathrm{EL2^0} = \mathrm{As^0_{Ga}} + (\mathrm{As}_i\mathrm{V}_{\mathrm{As}})^0$] described in Refs. 11 and 28:

$$\begin{aligned} &\mathrm{As_{Ga}}^0 + (\mathrm{As}_i\mathrm{V_{As}})^0 + 2(e+h) \to \mathrm{As_{Ga}}^+ + (\mathrm{As}_i\mathrm{V_{As}})^+ \\ &\quad + 3e + h \to \mathrm{As_{Ga}}^+ + 2e + h \\ &\quad + (\mathrm{As}_i\mathrm{V_{As}})^0 \to \mathrm{As_{Ga}}^0 + (\mathrm{As}_i\mathrm{V_{As}})^+ \\ &\quad + 2e + h \to \mathrm{As_{Ga}}^0 + (\mathrm{As}_i\mathrm{V_{As}})^0 + e + h. \end{aligned} \qquad (2)$$

The ultrafast Auger recombination rate depends on the charge state of the reconstructed interstitial arsenic (Figs. 2b and 3) and may be varied by altering the Fermi level position both in the course of the metastable transformation of the L2 center in accordance with Eq. (1), and on reduction in the degree of its compensation by various acceptors.[22,23] A striking illustration of these processes is the behavior of the zero-phonon line E_2 as a function of the concentration of the EL2^0 centers (Fig. 6a), and also the kinetic dependence under the metastable quenching conditions (Fig. 6b). In both cases the reported investigations were carried out on GaAs with the same concentrations of the EL2 centers, but with different concentrations of the acceptors, which would be equivalent to a change in the concentration of the EL2^0 centers. Clearly, the amplitude of the zero-phonon line E_2 first rises on reduction in the acceptor concentration and reaches its maximum for $N(\mathrm{EL2^0}) = 1.5\times10^{16}$ cm^{-3}. However, subsequently the concentration of the EL2^0 centers rose so much that the interstitial arsenic became filled with electrons and, consequently, the Auger recombination was strengthened and a steep fall of the amplitude of the zero-phonon line (Fig. 6a) was observed.

We can explain similarly the kinetic dependences in Fig. 6b. In the case of compensated GaAs:EL2 samples, when the duration of optical pumping with light of $h\nu = E_1$ energy is short, the amplitude of the zero-phonon line E_2 increases as a consequence of the increase in the concentra-

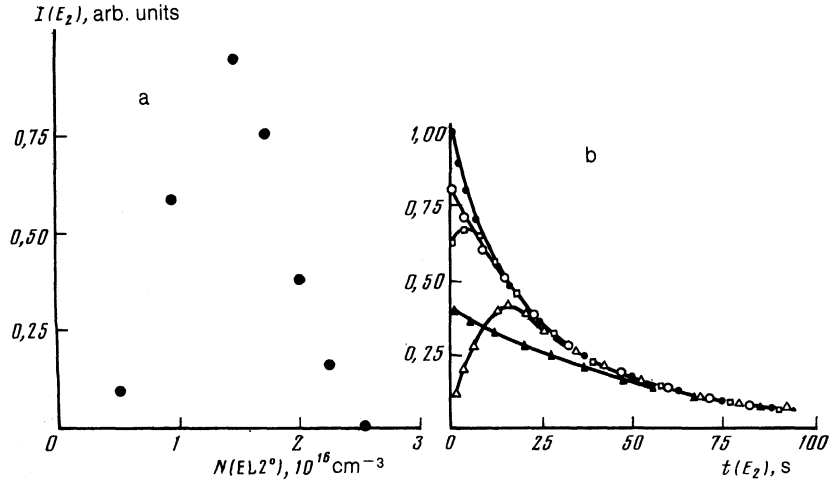

FIG. 6. a) Amplitude of the zero-phonon line (1.039 eV) of GaAs:EL2 plotted as a function of the concentration of the EL2^0 centers. b) Kinetics of quenching of the zero-phonon line (1.039 eV) in the course of the transition of the EL2 center to its metastable state [$t(E_2)$ is the quenching time of the zero-phonon line]: △) $N(\mathrm{EL2^0}) = 5\times10^{15}$ cm^{-3}; □) 1.0×10^{16} cm^{-3}; ●) 1.5×10^{16} cm^{-3}; ○) 1.7×10^{16} cm^{-3}; ▲) 2.0×10^{16} cm^{-3}; $h\nu = 1.18$ eV; $T = 4.2$ K.

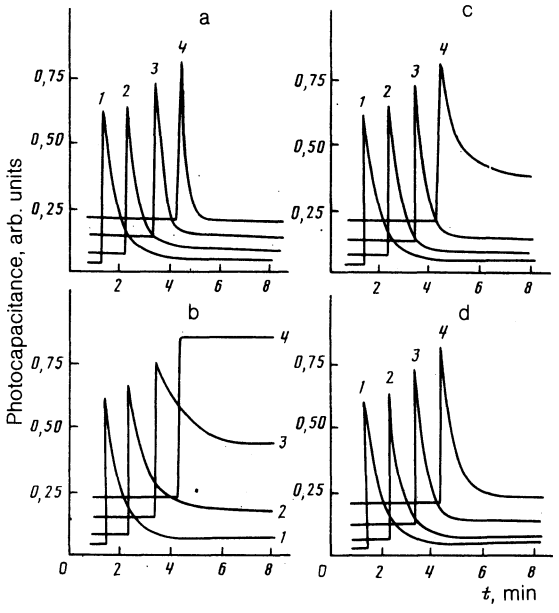

FIG. 7. Metastable quenching of the photocapacitance of GaAs:EL2 ($h\nu = 1.18$ eV, $T = 86$ K): a) $\vec{\mathscr{E}} \| [111]$; b) $\vec{\mathscr{E}} \| [\bar{1}\bar{1}\bar{1}]$; c) $\vec{\mathscr{E}} \| [100]$; d) $\vec{\mathscr{E}} \to [110]$. Value of $\mathscr{E}$: 1) 0.5×10^5 V/cm; 2) 1.0×10^5 V/cm; 3) 1.5×10^5 V/cm; 4) 2.5×10^5 V/cm.

tion of the $EL2^0$ centers [see Eq. (1)]. However, on attaining of a certain critical occupancy of the EL2 center with electrons, we find that the Auger recombination quenching of the zero-phonon line E_2 begins to dominate. For the same reason there is no initial rise in the kinetic dependences of the zero-phonon line obtained on investigation of weakly compensated GaAs:EL2 samples (Fig. 6b). Note that the kinetics of changes in the amplitude of the zero-phonon line E_2 in compensated GaAs:EL2 samples is an independent confirmation that the observed E_1 and E_2 optical transitions are due to the different charge states of the EL2 center.

Therefore, variation of the Fermi level in GaAs makes it possible to enhance or weaken the metastable properties of the EL2 center. Compensated GaAs:EL2 samples represent the optimal medium for the observation of the optical self-compensation of the EL2 centers [Eq. (1)]. As the degree of compensation of n-type GaAs:EL2 crystals decreases, the bulk of the EL2 centers is in the neutral state and, consequently, does not exhibit the metastable properties. Moreover, the observed mutual relationship between the Fermi level position and the metastable properties of GaAs:EL2 makes it possible to account for the absence of the metastability of the EL2 centers introduced in n-type GaAs by electron irradiation,[24] as well as for a strong reduction in the lifetime of nonequilibrium carriers on inversion from p-type to n-type conduction in GaAs crystals.[17]

A satisfactory check of the proposed mechanism of the metastability of the EL2 centers in GaAs is provided, on the one hand, by discovery of optical regeneration of the ESR spectra of the $EL2^+$ center using photons of energy $h\nu = E_g - E_1$ (Figs. 2c and 5):[25]

$$\left.\begin{aligned} D^{++} + h\nu(E_g - E_1) &\to D^+ + h, \\ D^0 + h &\to D^+, \end{aligned}\right\} \quad D^0 + D^{++} + h\nu(E_g - E_1) \to 2D^+, \tag{3}$$

and, on the other hand, by the good agreement between the experimentally determined energy of thermal annealing of the metastable state (≈ 0.34 eV)[10] and the height of the potential barrier hindering the $D^0 + 2h \to D^+ + h$ reaction (Fig. 2c), responsible for thermal regeneration of the D^+ state. Moreover, some contribution to the regeneration of the $EL2^+$ centers is made by an optical analog of this reaction (Fig. 2c):

$$D^0 + 2h + h\nu \to D^+ + h.$$

It was found experimentally that the capture of holes from the tail of the space-charge region is also responsible for regeneration of the photocapacitance of Schottky diodes made of GaAs:EL2, studied after the end of illumination with the pump light of $h\nu = E_1$ energy.[26] It should be pointed out that, in the case of optical pumping with light of the $h\nu = E_g - E_1$ energy, it is usual to find that about half of the original ESR signal of the $EL2^+$ centers is regenerated (Fig. 5), which is due to the partial capture of photoinduced holes by the compensating acceptor defects.[22,23]

It therefore follows that the mechanism of the metastability of the EL2 center is an optical analog of the negative-U reaction:

$$2D^+ + h\nu(E_1) \to D^0 + D^{++},$$

which, on the one hand, stimulates quenching of the ESR spectrum of the $EL2^+$ center and, on the other, results in strong reduction in the nonequilibrium-carrier lifetime, manifested by quenching of the interband photoconductivity, photocapacitance, and zero-phonon E_2 line in the absorption spectra of GaAs:EL2.

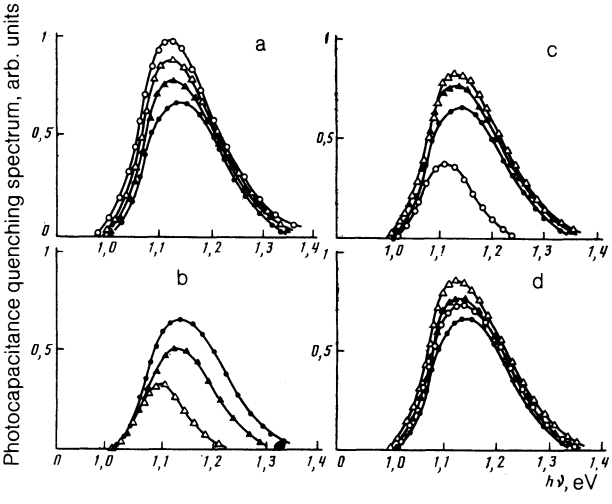

FIG. 8. Photocapacitance quenching spectra of GaAs:EL2 ($T = 86$ K) obtained in the following fields: a) $\vec{\mathscr{E}} \| [111]$; b) $\vec{\mathscr{E}} \| [\bar{1}\bar{1}\bar{1}]$; c) $\vec{\mathscr{E}} \| [100]$; d) $\vec{\mathscr{E}} \| [110]$. Value of $\mathscr{E}$: ●) 0.5×10^5 V/cm; ▲) 1.0×10^5 V/cm; △) 1.5×10^5 V/cm; ○) 2.5×10^5 V/cm.

Stark spectroscopy of the EL2 center in GaAs

The kinetic dependence of the quenching of the photocapacitance of GaAs:EL2 in the presence of different values of the anisotropic electric field is presented in Fig. 7. We can see that the orientation of the electric field $\vec{\mathscr{E}}$ may have both a stimulating and hindering influence on the transition of the EL2 center to a metastable state. This is manifested most clearly for the $\vec{\mathscr{E}} \| [111]$ and $\vec{\mathscr{E}} \| [\bar{1}\bar{1}\bar{1}]$ field directions (Fig.

7). In the former case, we observed acceleration of the photocapacitance quenching process on increase in the electric field, whereas in the latter case there was strong suppression of the metastable properties of the EL2 center. In other words, the Stark spectroscopy method, like piezospectroscopy, provided data identifying the EL2 center as a defect with C_{3v} symmetry. It should be pointed out that the results obtained were in good agreement with those determined by piezocapacitance spectroscopy[12] and by DLTS in the presence of anisotropic electric fields.[14]

A study of the photocapacitance kinetics of GaAs:EL2 using pumping light of different wavelengths made it possible to record the spectral dependence of the transition of the EL2 center to a metastable state (Fig. 8). The anisotropic influence of the electric field on the photocapacitance spectra indicated that the metastability mechanism was related to the symmetry of the EL2 center. The dynamics of the metastable transition in the presence of an external electric field can be described using a previous (Fig. 3) model of a tunnel deep defect allowing for the linear and quadratic Stark effects.[17] In this case the processes of charge transfer involving the EL2 center may be usefully considered by employing a three-dimensional system of adiabatic potentials, which—in contrast to the one-dimensional system (Figs. 2a and 2c, where $Q \| [111]$)—demonstrates clearly the Stark shifts of the charge states of the defect along different crystallographic axes (Fig. 9). The configurational coordinates Q_1, Q_2, and Q_3 join pairs of different charge states of the EL2 center (Fig. 3). In the absence of the electric field it was found that $Q_1 \| [111]$, $Q_2 \| [100]$, and $Q_3 \| [\bar{1}1\bar{1}]$; Q_1'' corre-

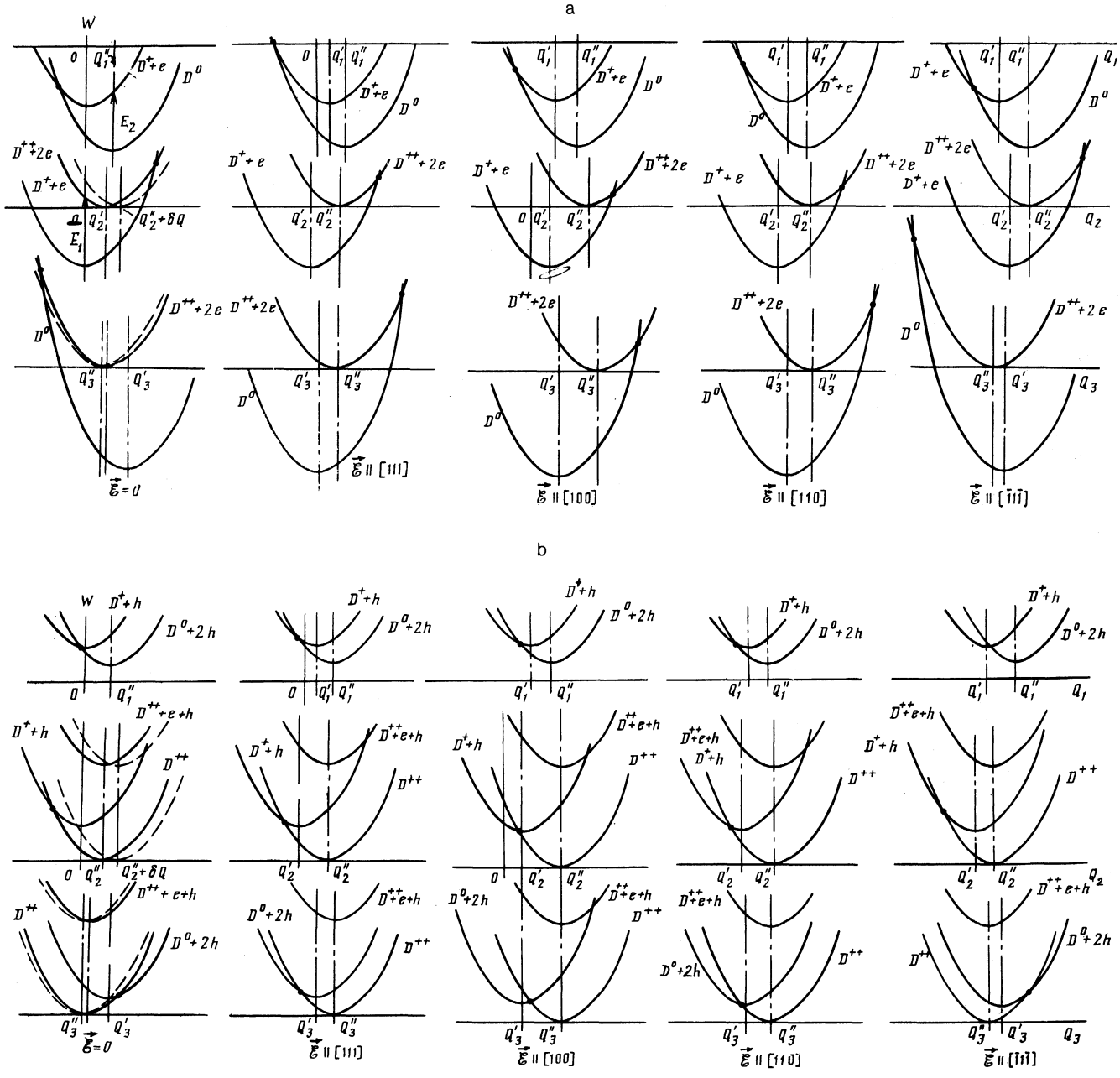

FIG. 9. Adiabatic potentials of different charge states of the EL2 center in GaAs in the case of defect–conduction band (a) and valence band–defect (b) optical transitions. The dashed curves ($\vec{\mathcal{E}} = 0$) represent the adiabatic potentials of the D^{++} state, corresponding to the position of an antisite center in a hexagonal interstice when the conditions are optimal for the optical ($+/++$) transition to the X valley of the conduction band.

sponds to the distance between the lattice site and a tetrahedral interstice, whereas $Q_2'' + \delta Q$ is the distance between a site and a hexagonal interstice. Figures 9a and 9b (lowest row) give the distance between the two types of interstices (Fig. 3). For $\vec{\mathscr{E}} \neq 0$ we have[17,18]

$$Q_1 \| [111] \cdot \cos(\vec{\mathscr{E}}, [111]), \quad Q_2 \| [100] \cdot \cos(\vec{\mathscr{E}}, [100]),$$
$$Q_3 \| [\bar{1}\bar{1}1] \cdot \cos(\vec{\mathscr{E}}, [\bar{1}\bar{1}1]).$$

The Stark shifts of the D^+ and D^{++} states of the EL2 center also depend on the orientation of the external electric field: $\delta Q' = \delta F'/\varkappa$ for D^+ and $\delta Q'' = 2\delta F''/\varkappa$ for D^{++}. Here, $\varkappa$ is the force constant and δF is the corresponding change in the electron–phonon interaction constant in the presence of an electric field:[17,18]

$$\delta F' = e\mathscr{E} \cos(\vec{\mathscr{E}}, [110]), \quad \delta F'' = e\mathscr{E} \cos(\vec{\mathscr{E}}, [100]).$$

In the absence of an electric field the energies E_2 and E_1 (Fig. 9) should agree completely with the intervalley splittings $\Delta_{L\Gamma}$ and $\Delta_{X\Gamma}$. Although in the case of the energy E_2 this hypothesis is satisfied quite well, the energy of the optical transition of the EL2 center to a metastable state $E_1 = 1.18$ eV was somewhat less than $\Delta_{X\Gamma}$. In accordance with the proposed model of a tunnel deep defect, the observed disagreement between the values of E_1 is optimally accounted for by postulating a Stark shift of the D^{++} state along the [100] axis (Fig. 3). Such Stark shifts may be due to compensating acceptors,[22,23] which occupy positions in the arsenic sublattice along the [100] axis relative to the EL2 center. The Stark shifts of the positions of the adiabatic potentials of the charge states of the EL2 center under the conditions of an anisotropic electric field (Fig. 9) describe well the behavior of the corresponding photocapacitance quenching spectra (Fig. 8). An increase in the electric field $\vec{\mathscr{E}} \| [111]$ enhances the photocapacitance quenching, which is accompanied by some broadening of the corresponding spectral dependence (Fig. 8a). This field dependence of the probability of an optical transition of the EL2 center in a metastable state is due to an increase in the probability of two-electron capture[17] and activation of the Auger processes in a field $\vec{\mathscr{E}} \| [111]$ (Fig. 9). Some shift of the maximum in the photocapacitance quenching spectrum could obviously be explained by a reduction in the energy E_2, known to influence the spectral dependence indirectly under optical self-compensation conditions.

The behavior of the photocapacitance quenching spectra in the $\vec{\mathscr{E}} \| [\bar{1}\bar{1}1]$ case is just the opposite (Fig. 8b). In this case there is a strong reduction in the probability of two-electron capture and of the Auger recombination of nonequilibrium carriers (Fig. 9). The field shift of the quenching maximum toward lower energies (Fig. 8b) is due to a corresponding reduction in the energy E_1 (Fig. 9). Other variants of the influence of an anisotropic electric field on the photocapacitance quenching spectrum for $\vec{\mathscr{E}} \| [100]$ and $\vec{\mathscr{E}} \| [110]$ (Figs. 8c and 8d) demonstrate clearly the nonmonotonic kinetics of changes in the probabilities of the investigated processes of the transition of the EL2 center to the metastable state, depending on the values of the corresponding Stark shifts.

It therefore follows that the use of Stark spectroscopy in the presence of an anisotropic electric field in GaAs enabled us to identify the C_{3v} symmetry of the EL2^0 center and to demonstrate that the D^0, D^+, and D^{++} states correspond, respectively, to the L, Γ, and X conduction-band valleys. An anisotropic electric field controls nonequilibrium carrier recombination and the optical self-compensation of the EL2 center, which is accompanied by the tunneling of its antisite component in the GaAs lattice.

4. CONCLUSIONS

The results of the photo-ESR, piezospectroscopy, and Stark spectroscopic investigations indentify the EL2 center in GaAs as a double donor with the C_{3v} symmetry (EL2 = $As_{Ga} + As_i V$) and charge states D^0, D^+, and D^{++}, respectively, formed from the wave functions of the L, Γ, and X conduction-band valleys. Recombination of nonequilibrium carriers in GaAs:EL2 and the process of optical charge exchange involving the EL2 centers are accompanied by tunneling of its anti-site component As_{Ga} between the lattice sites (D^+ state) to the tetrahedral (D^0 state) and hexagonal (D^{++} state) interstices.

Our results demonstrated that the mechanism of the metastability of the EL2 center has one underlying factor, which is the optical analog of the negative-U reaction $2D^+ + h\nu(E_1) \rightarrow D^0 + D^{++}$, inducing tunneling of an antisite defect from a regular site to a tetrahedral interstice. On the one hand, the transition to the metastable state stimulates quenching of the ESR spectrum of the EL2$^+$ center and, on the other, it reduces strongly the nonequilibrium carrier lifetime manifested by quenching of the interband photoconductivity, photocapacitance, and zero-phonon line (1.039 eV) in the absorption spectra of GaAs:EL2. It was found that the temperature and rate of annealing of the metastable neutral state of EL2 are governed by the energy barrier of the reaction $D^0 + h \rightarrow D^+$. Variation of the Fermi level position influences the degree of electron occupancy of interstitital arsenic, which is responsible for the Auger processes of quenching of the characteristics of GaAs:EL2. It is therefore possible to enhance or weaken the metastable properties of the EL2 center.

It was found that an anisotropic electric field induces corresponding Stark shifts at the positions of the charge states of the EL2 center, which exhibit a change in the probability of the processes of self-compensation of the center and make it possible to control within wide limits the process of recombination of nonequilibrium carriers in GaAs.

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