The EL2 center in GaAs: symmetry and metastability

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Classification
Physics Abstracts
71.55F — 72.40 — 78.20H

Proofs not corrected by the author

The EL2 center in GaAs : symmetry and metastability

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(*Received 22 May 1991, accepted 12 June 1991*)

Abstract. — Photo-EPR, piezospectroscopic and Stark-effect photocapacitance data were used to determine the symmetry of the EL2 center in GaAs and to identify the mechanism that underlies its metastable behavior. The results unambiguously point to C_{3V} as the type of symmetry for this antisite double donor whose charge states — $D^+ = As_{Ga}$, $D^0 = (As_iV_{Ga})^0$ and $D^{++} = (As_iV_{Ga})^{++}$ — occupying, respectively, the positions on the site and in the tetrahedral and hexagonal interstices, are brought about, in the same order, by the wavefunctions of the Γ, L and X valleys of the conduction band. The transition made by the EL2 center to a metastable state is the result of a charge exchange of the type $2D^+ + h\nu \rightarrow D^0 + D^{++}$, which causes the antisite As_{Ga} defect to tunnel from its position at the site to a position in the tetrahedral interstice. Annealing of the center in this state proceeds at such temperatures and rates as are determined by the height of the energy barrier to the $D^0 + h \rightarrow D^+$ reaction.

1. Introduction.

The EL2 center, a deep double donor with the D^0/D^+ level located at $E_c - 0.75$ eV and the D^+/D^{++} level at $E_v + 0.52$ eV, has recently been the subject of great interest in GaAs research because of the evidence [1] that its presence in single crystals and epitaxial layers makes the material semi-insulating while at the same time promoting high carrier mobility. Based on the complete correlation between the spectral dependences of metastable quenching obtained for the photocapacitance, photoconductivity and EPR triad in GaAs with EL2 [1-4], the center's core has been identified as an antisite As_{Ga} double donor. The quenching is the result of the reduction experienced by the lifetime of photoexcited carriers as, according to the hypothesis proposed by Dabrowski and Scheffler [5], and Chadi and Chang [6], neutral antisite donors shift to occupy the tetrahedral interstitial position under irradiation with $h\nu = 1.0$-1.3 eV light : $As^0_{Ga} + h\nu \rightarrow (As_iV_{Ga})^0$. This photoexcited state of the EL2 center is metastable at $T < 140$ K, which is why the material does not regain its original properties on stopping illumination with pumping light [1-3].

As its other distinctive characteristic, the EL2 center in GaAs has revealed three features in its absorption coefficient spectral dependence. Photocapacitance spectroscopic studies have shown these features, which occur at 0.8 eV, 1.0 eV and 1.3 eV, to be due to optical electron

transitions between the EL2 level and, respectively, the Γ, L, X valleys of the conduction band [1, 2]. An alternative explanation of these features as arising from the intercenter transitions experienced by the EL2 center was offered, however, by subsequent researchers who were reportedly unable, using their experimental setup, to detect the zero-phonon line ($E = 1.039$ eV) revealed by the absorption spectra in the corresponding spectral dependences for the photocurrent [7-9]. The zero-phonon line was also found [9] to disappear in the course of preliminary illumination with $h\nu = 1.0$-1.3 eV pumping light, and this fact could not but be interpreted as additional evidence that the optical transitions responsible for the transformation of the EL2 center to a metastable state are of the intercenter nature.

The first determination of the EL2 center symmetry was made during an investigation of the splittings observed in the above zero-phonon line, performed under uniaxial stress applied to single crystals of GaAs : EL2 (Ref. [9]). A conclusion was made that the EL2 center is an isolated As_{Ga} defect with T_d symmetry. This conclusion, however, was not borne out by later EPR, ENDOR and piezocapacitance spectroscopic studies which suggested the EL2 center to be, instead, an $As_{Ga} + As_i$ complex with C_{3V} symmetry [10-12].

Thus, the question of the mechanism for EL2 center metastability and the problem of EL2 center symmetry in GaAs are far from being resolved ; particularly, in those aspects which concern the determination of the relative contribution of intercenter and interband transitions to the above-described process of metastable quenching. It is timely to return to the issue now that the zero-phonon line at 1.039 eV has eventually been detected in the spectral dependence of the photo-current [13]. More important, the coincidence revealed by the EPR and photocapacitance quenching spectra in GaAs : EL2 is paradoxical when viewed through the current models for the EL2 center (see Refs. [1, 2, 5, 6, 9-11]). The paradox is that the former process has to be attributed to the reduction in the concentration of paramagnetic As^{+}_{Ga} centers [2, 10], whereas the latter should necessarily be regarded as due to the transition made by the As^{0}_{Ga} center to the metastable state [1, 2, 5, 6]. The paradox can be resolved either by assuming that the antisite donor in GaAs has two neutral states — one, the ground state, on the site, and the other, the excited state, in the tetrahedral interstice, or by accepting C_{3V} symmetry as the only possible symmetry for the neutral state of the As_{Ga} center. If the latter is true, then the metastability mechanism for the EL2 center would be related not to the intercenter transitions, but to the charge exchange processes of the $As^{+}_{Ga} \rightarrow (As_i V_{Ga})^0$ type, which must induce the defect to tunnel between the position on the site and the other position in the terahedral interstice.

The model for the EL2 center proposed below results from a comprehensive study of the anisotropic nature of the influence that the electric field exerts on photocapacitance quenching ; the other input has been provided by the optical absorption data recorded in material subjected to both hydrostatic pressure and uniaxial stress. A relationship is demonstrated between the metastability properties and symmetry possessed by the charge states of the deep defect and the structure of the conduction band.

2. Experiment.

Piezospectroscopic measurements of optical transmission were made at 4.2 K under hydrostatic pressure and uniaxial stress applied to Bridgemen-grown n-type (with $n \simeq 1.5 \times 10^{16}\,cm^{-3}$ at 77 K) GaAs single crystal samples cut to dimensions $3 \times 3.5 \times 7\,mm^3$. The uniaxial stress was applied to the long axis which was parallel to the [111], [100], or [110] direction. Light with both parallel and perpendicular polarization relative to the stress direction was used. The intensity of the monochromatic light was kept at a low level, so as to prevent the transition of the centers to the metastable state.

A higher intensity ($h\nu = 1.0$-1.3 eV) of the pumping light was used in the investigation of

the EL2 metastability transition in order to get the photocapacitance, the 1.039 eV zero-phonon line, and the corresponding EPR spectrum gradually quenched. The time dependence of the zero-phonon line quenching was studied against the position of the Fermi level as determined by the degree of EL2 center compensation. This allowed the information about the quenching and regeneration of EL2 characteristics to be extracted from the spectra recorded, and the role of the center's two components (double antisite donor and interstitial arsenic atom) in recombination of nonequilibrium carriers in GaAs of p- and n-type conductivity to be defined.

The photocapacitance investigations were also employed to determine the EL2 center symmetry. This was made possible by extending the method of capacitance spectroscopy to piezocapacitance and Stark-effect measurements. While the standard technique can only provide information on the energy characteristics of a point defect but is unable to locate it in the crystal lattice, the piezo- and Stark-effect versions can perform this function very well and they also permit an investigation of the capacitance signal against the direction in which uniaxial stress [12] or electric field [13] is applied relative to the crystallographic axes of the GaAs : EL2 single crystal. The present work, therefore, used a photocapacitance analog of the Stark-effect spectroscopy to study the relationship between EL2 metastability properties and the center's symmetry. The Schottky-barrier diodes employed for the study were fabricated by depositing gold on the face perpendicular to the 7 mm length of Cz-GaAs single crystals (measuring 1.3 mm and 1.5 mm in height and width, respectively), which was oriented along [111], [100], [110], or $[\bar{1}1\bar{1}]$ direction. The electric field in the diode could thus be oriented strictly along the selected crystallographic axis. The uniformity in the distribution of free electrons, with concentration of $1.0\text{-}1.5 \times 10^{16}\,\mathrm{cm}^{-3}$, supplied by the tellurium impurity contained in the as-grown crystals, was monitored *via* CV measurements.

Metastability-induced quenching of the photocapacitance signal was recorded at various values of the electric field present in the samples illuminated with monochromatic light. The time dependences thus obtained were used to determine the photocapacitance quenching spectra for different directions of the applied electric field relative to the crystallographic axes of Cz-GaAs : EL2 samples.

3. Results and discussion.

3.1 PIEZOSPECTROSCOPIC INVESTIGATION OF THE EL2 CENTER IN GaAs. — The optical absorption spectra obtained are shown in figures 1a and b. These enable the variation in the energy of the 1.039 eV zero-phonon line and the optical transition of the EL2 center to the metastable state (1.18 eV) to be determined as a function of the applied hydrostatic pressure (Fig. 1c). As the pressure increases, the optimal energy of transition to the metastable state E_1 decreases (the 1.0-1.3 eV line), while the zero-phonon line E_2 shifts to higher energies. The separation of the phonon replicas, though, remains unaffected. These results, which are in good agreement with results reported in the literature [15], show that E_1 and E_2 optical transitions are associated with different charge states of the EL2 center in GaAs. It can be seen in figure 1c that ΔE_1 and ΔE_2 agree well with the corresponding changes in the energy difference between the valleys of the conduction band in GaAs : $\Delta E_1 = \Delta_{X\Gamma}(p)$, $E_2 = -\Delta_{L\Gamma}(p)$ [16].

The observed relationship between the optical transitions and the structure of the conduction band can be explained with a model for a deep center which postulates a nonmonotonic dependence of the electron-vibrational interaction constant on the charge and spin states [17, 18] (Fig. 2). In the model, a deep defect is a tunneling center whose different charge states occupy lattice positions of different symmetry, so that each belongs to a specific

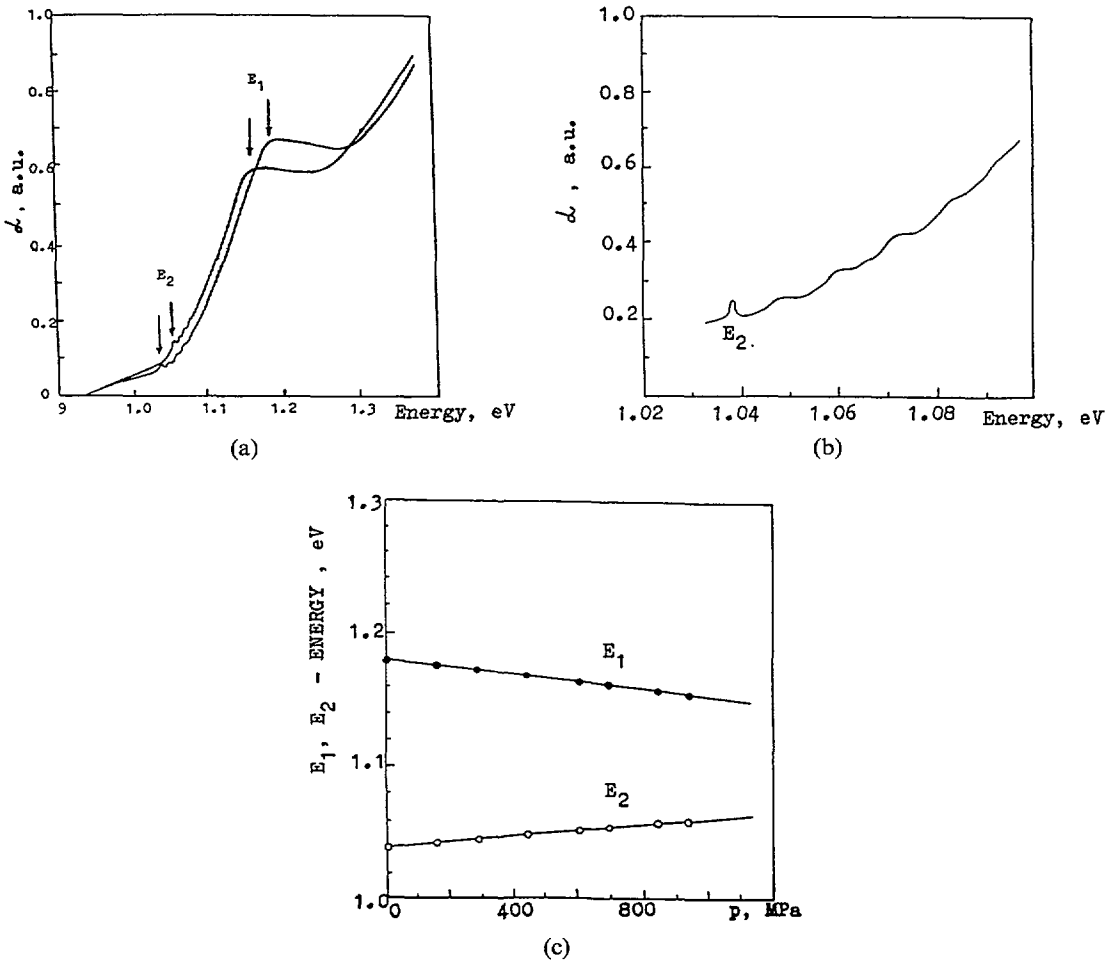


Fig. 1. — GaAs : EL2. (a) Optical absorption spectrum. $p = 0$ (1) ; $p = 950$ MPA (2) ; arrows mark the position of the optical transition to the metastable E_1 state and the location of the zero-phonon line. (b) A section of the optical absorption spectrum showing the zero-phonon line E_2. (c) Energy of the optical transition to the metastable E_1 state and of the zero-phonon E_2 line as a function of the hydrostatic pressure applied to the crystal. The dependences calculated from reference [16] are given as solid lines.

valley of the conduction band. Applied to the EL2 center in GaAs, the model has the D^+ state occupying the substitutional position and resulting from the wave-functions of the Γ valley, whereas the D^0 and D^{++} states are located respectively in the tetrahedral and hexagonal interstices, and belong — in the same order — to the L and X valleys of the conduction band (Figs. 2, 3). It then follows that the $D^0 = (As_iV_{Ga})^0$ state has the C_{3V} symmetry, and also that the EL2 level is the product of the wavefunctions generated by the L valley. This being so, the D^+ and D^{++} states must have, respectively, the T_d and D_{2d} symmetries. In practice, however, the symmetry of the D^+ state is reduced to C_{3V} because of the reconstruction of the nearest arsenic site to As_iV_{As} (Fig. 3), as indicated by the ENDOR data which identify the EL2 center as an $As_{Ga} + As_i$ complex [11]. Though for a different reason, the symmetry of the D^{++} stats will likewise tend to become C_{3V} — due to the Stark effect induced by the presence of compensating acceptors [17]. The $D^0 \rightarrow D^+$ optical

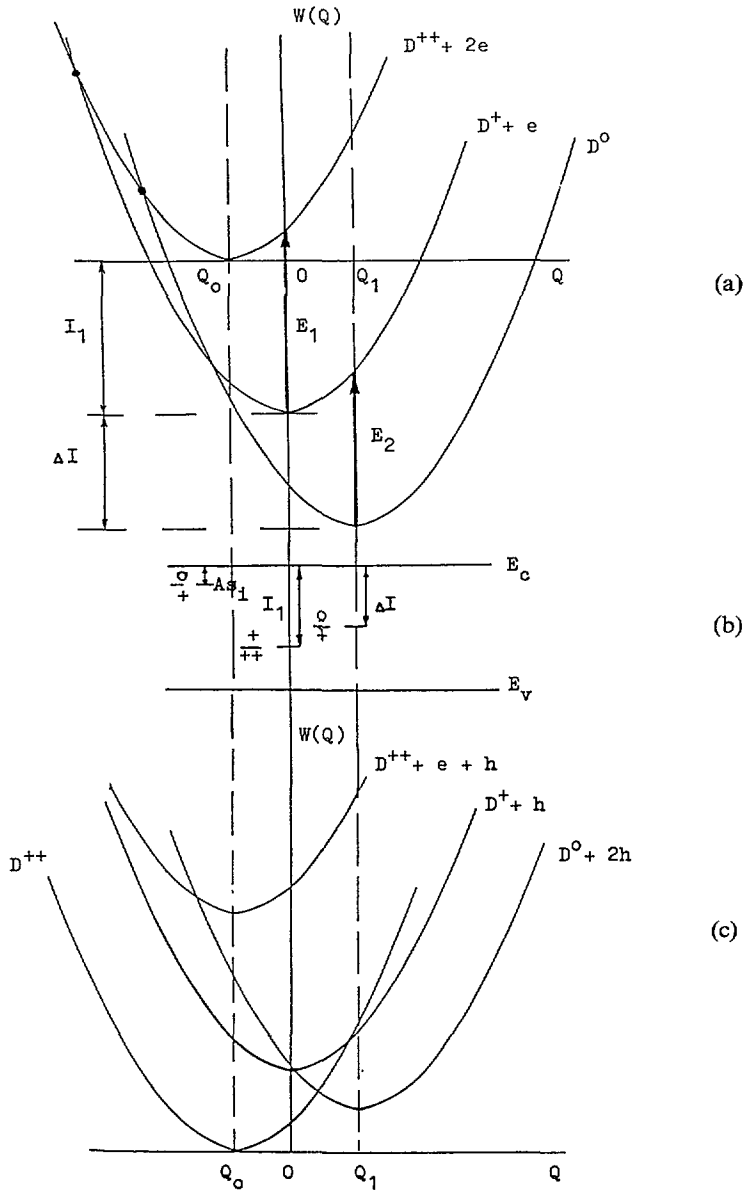


Fig. 2. — Adiabatic potentials for different charge states of the EL2 center in GaAs ; (a) optical transition made by a defect to the conduction band ; (b) an equivalent one-electron band scheme ; (c) optical transition from the valence band to a defect ; $I_2 = I_1 + \Delta I$; $Q \parallel [111]$.

transition, whose energy optimum is given by the zero-phonon line of figure 2a, is therefore a tunneling process whereby the EL2 center changes its tetrahedral interstitial position for a substitutional position, causing the electron that has, as a result, been excited from the EL2 level to the L valley to undergo intervalley scattering : $\Delta E_2 = -\Delta_{L\Gamma}(p)$. Figure 1c shows that the above sequence of events takes place in its purest form under application of the hydrostatic pressure. The intervalley scattering is also the fate of the electron which is photoexcited to the Γ valley as a result of the D^+/D^{++} transition : $\Delta E_1 = \Delta_{X\Gamma}(p)$.

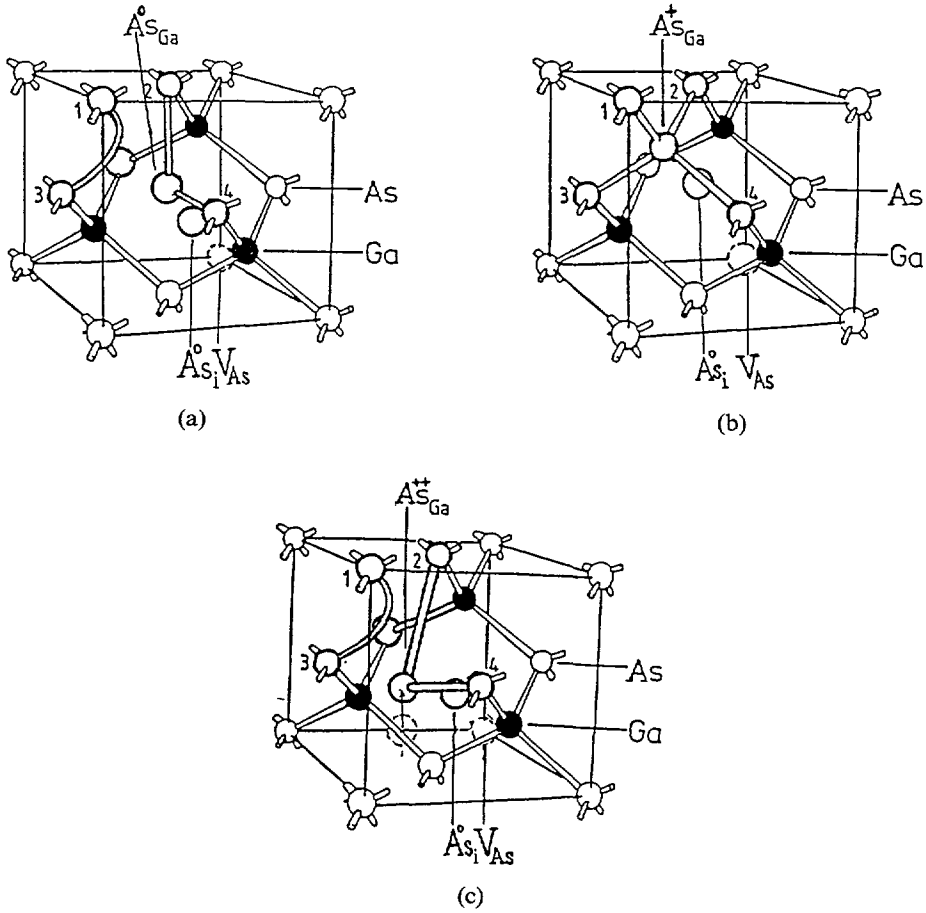


Fig. 3. — Suggested model for the EL2 center in GaAs : (a) D^0 state ; (b) D^+ state ; (c) D^{++} state.

Figure 4 shows that the structure of the conduction band is also a factor in optical absorption of uniaxially stressed GaAs : EL2 single crystals. The greatest splitting of the zero-phonon line is observed for the stress applied to the [111] axis. In contrast, no splitting of the E_2 line was observed [11] when the stress was applied in the [100] direction, while the condition $\sigma \| [110]$ gave rise to three components which interacted in a manner suggestive of the Jahn-Teller effect. It should be noted that in the measured samples the direction of the applied stress must be aligned accurately with the [100] axis. Otherwise, an « admixture » of the stress applied to the [111] axis will inevitably lead to a slight splitting of the zero-phonon line, which is what was apparently observed in reference [9]. See figure 4b.

The splittings induced in the spectral lines of allowed transitions that occur in cubic crystals containing centers with different symmetries have been calculated by Kaplyanskii [19]. Providing a means of identifying a given center's symmetry, these calculations are based on such criteria as intensity, polarization degree, the number of resultant components, and the amount of the shift relative to the basic line. When interpreted in light of these criteria, the results obtained in the present work point out unambiguously to the C_{3V} symmetry for EL2 centers in GaAs. In its entirety, the picture of the zero-phonon line splittings is in good accord

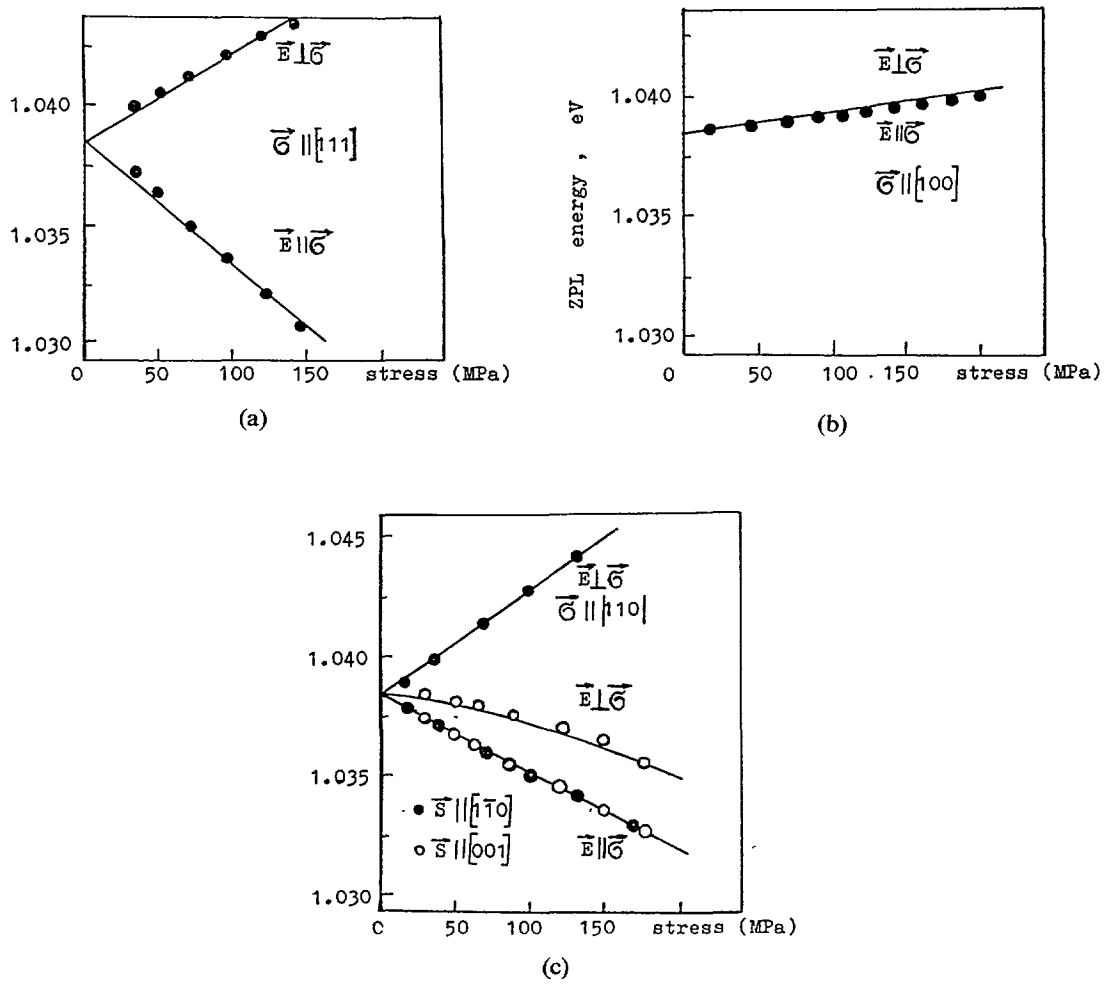


Fig. 4. — Energy of the zero-phonon line as a function of uniaxial stress. The solid line in (b) shows the $|1/3 \cdot \Delta_{L\Gamma}(p)|$ dependence as yielded by the results of reference [20].

with the results of « hot photoluminescence investigations of the effect produced by uniaxial stress on the splitting of the L valley [20]. Figure 4b shows that the shift of the zero-phonon line under $\sigma \| [100]$ is equal to $-1/3 \times \Delta_{L\Gamma}$. This constitutes independent evidence that the EL2 level belongs to the L valley and accounts for the presence of the zero-phonon line in the spectral dependence of the photocurrent [13].

Thus, the study of optical absorption in GaAs single crystals subjected to hydrostatic pressure and uniaxial stress has shown that the D^0, D^+ and D^{++} states of the EK2 center have the C_{3V} symmetry and are due, respectively, to the L, Γ, and X valley of the conduction band.

3.2 QUENCHING AND REGENERATION OF EPR DUE TO $EL2^+$ CENTER IN GaAs. — As intensive optical pumping at $h\nu = E_1$ continues for some time, two-electron capture becomes the dominant process [17], and the residual concentration of singly charged EL2 centers

transforms to a metastable state (Fig. 2a):

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

The process is an optical analog of the negative-U reaction [17, 18, 21] and it accounts for the situation in which the EPR due to $EL2^{+}$ centers undergoes quenching in the range of $h\nu = 1.0\text{-}1.3$ eV (see Fig. 5) while the concentration of the $EL2^{0}$ centers experiences a rise. Yet, as two pairs of figures 5-6 and 7-8, demonstrate, the effect of optical pumping with $h\nu = E_1$ light is to suppress rather than enhance the E_2 line or photocapacitance, with the amount of quenching being, at first glance, proportional to the concentration of $EL2^{0}$ centers. This paradox, already mentioned, is due to a drastic reduction of the nonequilibrium carrier lifetime because of intense Auger recombination that takes place as EL2 centers are filled with electrons ($EL2^{0} = As^{0}_{Ga} + (As_iV_{As})^{0}$) [11, 18]:

$$\begin{array}{l} As^{0}_{Ga} + (As_iV_{As})^{0} + 2(e + h) \rightarrow As^{+}_{Ga} + (As_iV_{As})^{+} + 3\,e + h \rightarrow \\ As^{+}_{Ga} + (As_iV_{As})^{0} + 2\,e + h \rightarrow As^{0}_{Ga} + (As_iV_{As})^{+} + 2\,e + h \rightarrow \\ As^{0}_{Ga} + (As_iV_{As})^{0} + e + h\,. \end{array} \qquad (2)$$

The rate of hyperfast Auger recombination is determined by the charge state of the reconstructed interstitial arsenic atom (Figs. 2b and 3); so, it can be controlled either by causing the Fermi level to change its position in the course of transition by EL2 centers to the metastable state (1), or through lowering the compensation degree of EL2 centers by varying the amount of added acceptors [22, 23]. An instructive illustration of these processes is provided by the behavior of the zero-phonon line in the presence of increasing concentrations of $EL2^{0}$ centers (Fig. 6a), and also by its time dependence under the conditions of metastable quenching (Fig. 6b). In both cases, the GaAs samples under investigation had equal content of EL2 centers, but differed in acceptor concentration, i.e. in the concentration of $EL2^{0}$ centers. In the experiment, the amplitude of the E_2 line first showed an increase with decreasing acceptor concentration, reaching a maximum at $EL2^{0} = 1.5 \times 10^{16}\,cm^{-3}$ Above this concentration, the arsenic atoms begin to get filled with electrons, which causes the Auger-recombination process to intensify and, as a consequence, leads to a sharp reduction in the E_2 line amplitude (Fig. 6a).

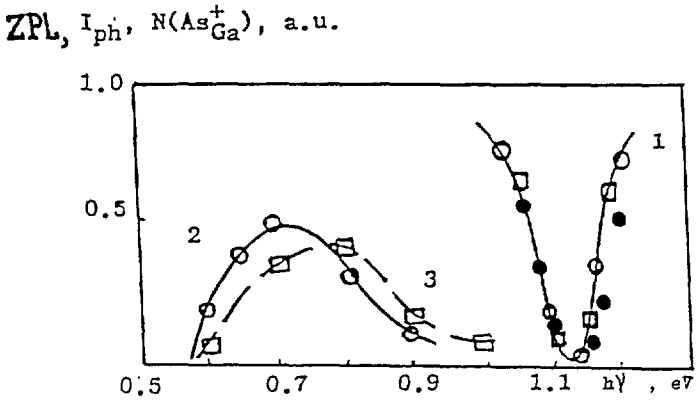


Fig. 5. — Quenching of the 1.039 eV zero-phonon line, bandgap photoconductivity, and EPR of the AS^{+}_{Ga} centers (1); subsequent regeneration of bandgap photoconductivity (2) and of As^{+}_{Ga} EPR (3) in GaAs : EL2.

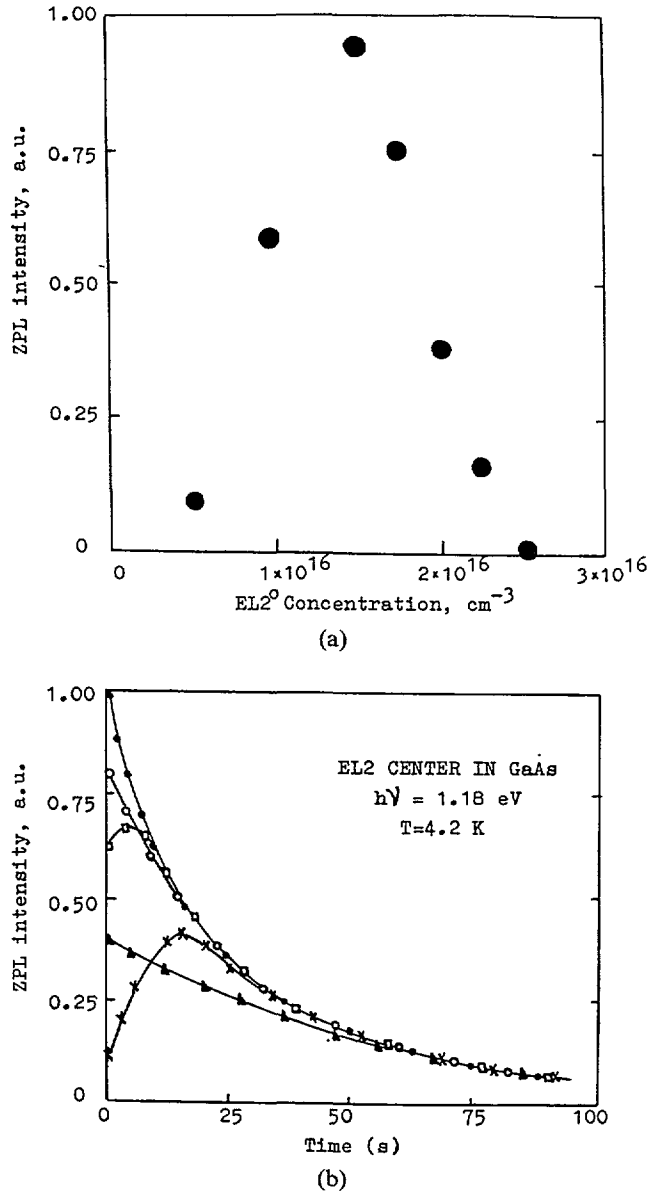


Fig. 6. — Zero-phonon line intensity as a function of the D^0 state ; (b) The time dependence of zero-phonon line quenching taken during the transition of the EL2 center to a metastable state : (×) $N(EL2^0) = 5 \times 10^{15}\,cm^{-3}$; (□) $1.0 \times 10^{16}\,cm^{-3}$; (•) $1.5 \times 10^{16}\,cm^{-3}$; (○) $1.7 \times 10^{16}\,cm^{-3}$; (▲) $2.0 \times 10^{16}\,cm^{-3}$

The same explanation holds for the time dependences, shown in figure 6b. The amplitude of the E_2 line recorded in compensated samples of GaAs : EL2 which received small doses of illumination with $h\nu = E_1$ pumping light is seen to increase as the concentration of $EL2^0$ centers would, according to (1), increase. As before, once a certain level in the filling of EL2 centers by electrons is reached, Auger recombination come to the fore, and the zero-phonon line undergoes quenching. For this same reason, the initial portion of the

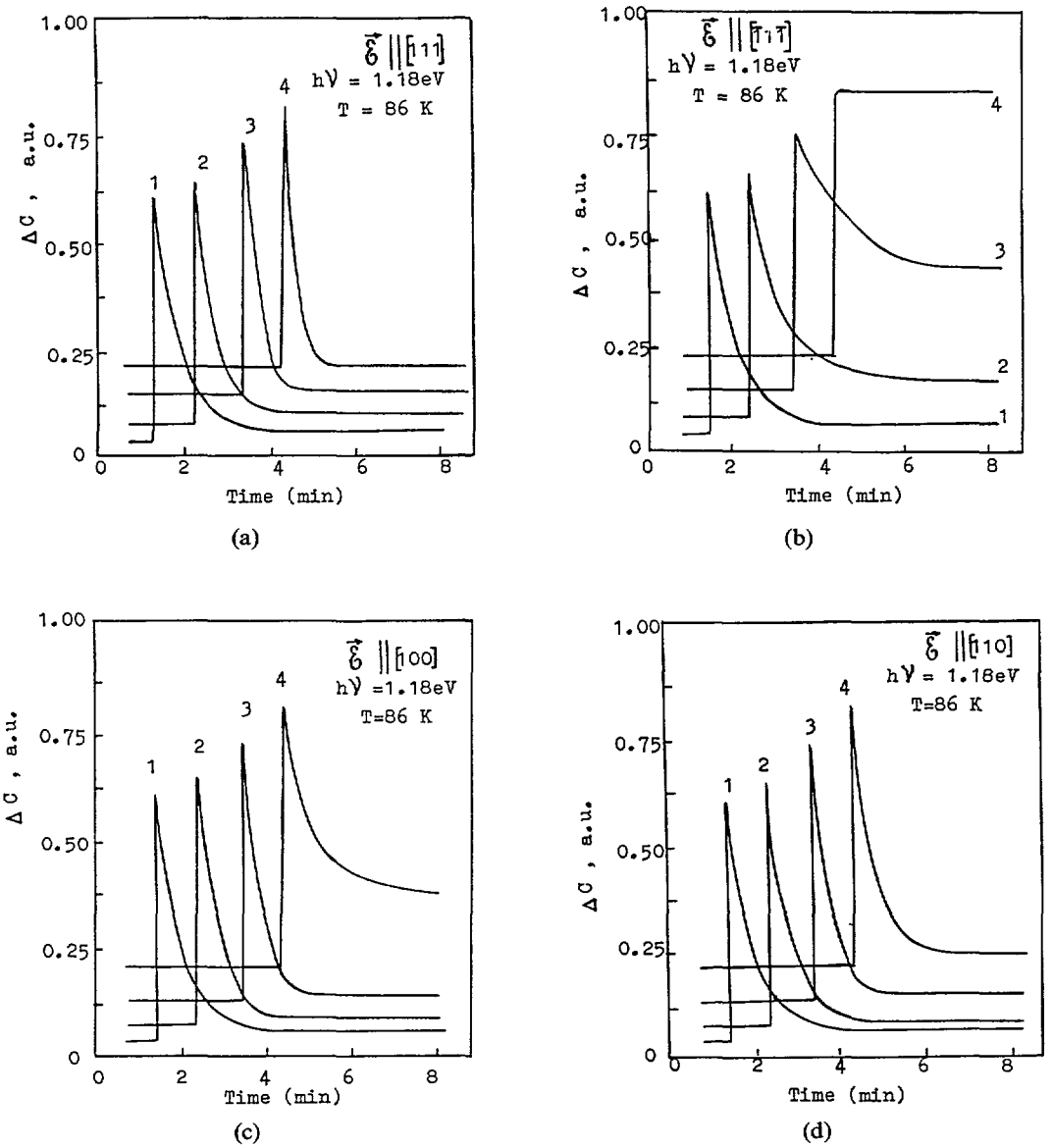
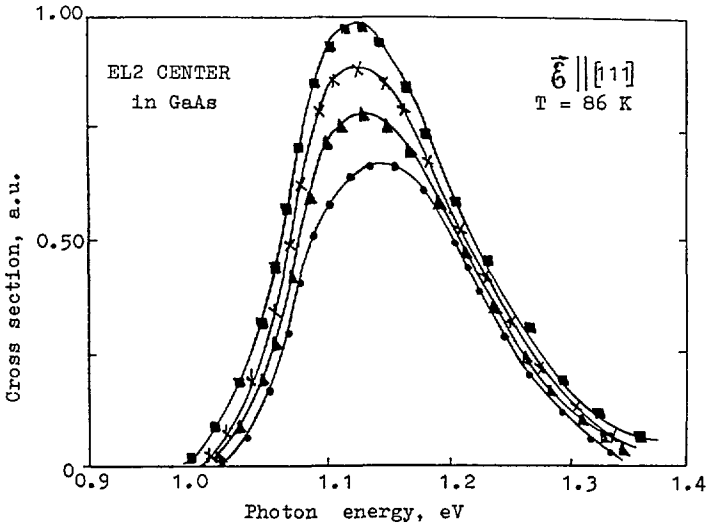


Fig. 7. — Photocapacitance quenching as it occurs in the EL2 center in GaAs : (a) $\mathcal{E} \| [111]$, (b) $\mathcal{E} \| [\bar{1}1\bar{1}]$, (c) $\mathcal{E} \| [100]$, (d) $\mathcal{E} \| [110]$. 1) $\mathcal{E} = 0.5 \times 10^5$ V/cm ; 2) $\mathcal{E} = 1.0 \times 10^5$ V/cm ; 3) $\mathcal{E} = 1.5 \times 10^5$ V/cm ; 4) $\mathcal{E} = 2.5 \times 10^5$ V/cm.

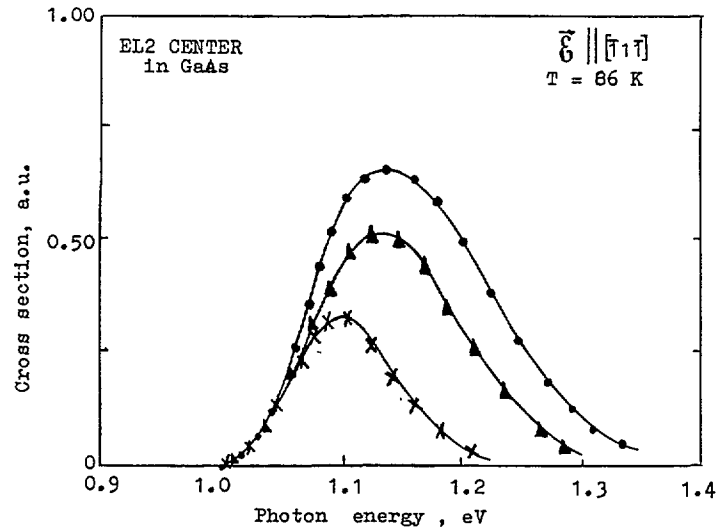
E_2 time dependence curve obtained for the weakly compensated GaAs : EL2 samples lacks the usual ascent (Fig. 6b). An additional value of the time dependences describing the behavior of E_2 amplitude in compensated GaAs : EL2 samples lies in providing independent confirmation of the above demonstrated origin of E_1 and E_2 optical transition from different charge states of the EL2 center.

Thus, by varying the position of the Fermi level in GaAs, it is possible to enhance or depress the metastability properties of the EL2 center. Compensated GaAs : EL2 samples

probably provide the best medium in which to carry out observations of optical self-compensation processes as these take place on EL2 centers, see (1). The presence or absence of metastability in a given n-type GaAs : EL2 single crystal is a measure of the degree of compensation in this crystal : at low degrees of compensation there can be no metastability as the majority of EL2 centers are in the neutral state. The observed relationship between the

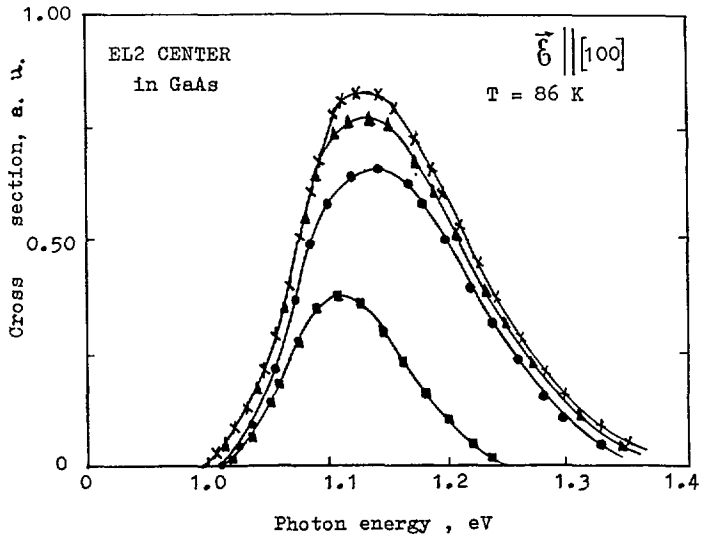


(a)

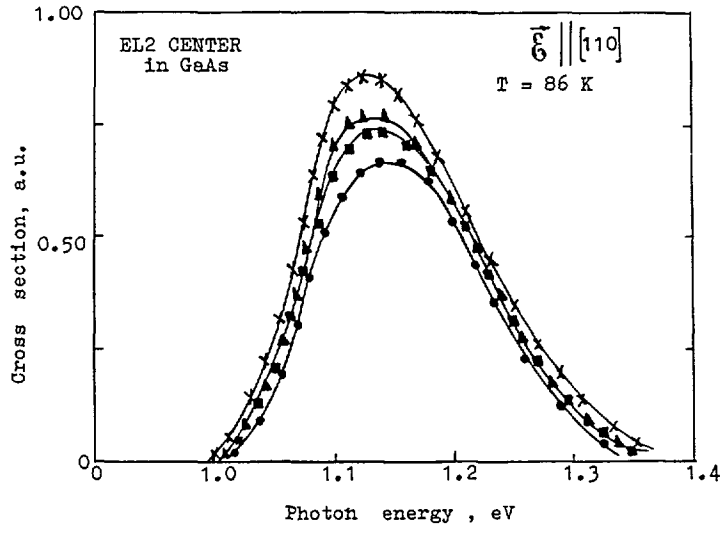


(b)

Fig. 8. — Rate of optical transition of the EL2 center to the metastable state : (a) $\mathcal{E} \| [111]$, (b) $\mathcal{E} \| [\bar{1}1\bar{1}]$, (c) $\mathcal{E} \| [100]$, (d) $\mathcal{E} \| [110]$. (○) 0.5×10^5 V/cm ; (▲) 1.0×10^5 V/cm ; (×) 1.5×10^5 V/cm ; (◆) 2.5×10^5 V/cm.



(c)



(d)

Fig. 8 (*continued*).

position of the Fermi level and metastability of GaAs : EL2 is also very helpful — for instance, in explaining the demonstrated lack of metastability in n-type GaAs single crystals containing EL2 centers that were introduced along with electron irradiation of the crystals [24] or the observed drastic reduction of nonequilibrium carrier lifetime that accompanies a switch from the p- to n-type conductivity in GaAs single crystals [17].

Confirmation of the adequacy of the proposed mechanism of EL2 metastability in GaAs has been provided by (i) an experimental observation of $EL2^+$ center EPR regeneration at

$h\nu = E_g - E_1$ (Figs. 2c and 5) [25] :

$$\left.\begin{array}{l} D^{++} + h\nu\,(E_g - E_1) \rightarrow D^{+} + h \\ D^{0} + h \rightarrow D^{+} \end{array}\right\| D^{0} + D^{++} + h\nu\,(E_g - E_1) \rightarrow 2\,D^{+} \qquad (3)$$

and (ii) by good agreement between the experimentally determined thermal anneal energy for the metastable state, which turned out to be 0.34 eV (Ref. [10]), and the height of the energy barrier for the $D^0 + 2\,h \rightarrow D^+ + h$ reaction (see Fig. 2c), the main vehicle of the thermal regeneration process involving the D^+ state. The other contributor to $EL2^+$ EPR regeneration is this reaction's optical analog, of the form : $D^0 + 2\,h + h\nu \rightarrow D^+ + h$. The capture of holes from the « tail » of the space charge region has also been shown [26] to contribute to regeneration of photocapacity in GaAs : EL2 Shottky-barrier diodes on removing illumination with $h\nu = E_1$ pumping light. As can be seen in figure 5, application of optical pumping with $h\nu = E_g - E_1$ usually recovers about one half of the original $EL2^+$ EPR signal — due to the capture of a part of photoinduced holes on the compensating acceptor defects [22, 23].

In conclusion, the EL2 center metastability mechanism is based on an optical analog of the negative-U reaction : $2\,D^+ + h\nu\,(E_1) \rightarrow D^0 + D^{++}$ While stimulating the $EL2^+$ EPR quenching, this reaction leads, at the same time, to a drastic reduction of the nonequilibrium carrier lifetime, an effect which is reflected in the quenching of intervalley photoconductivity, photocapacitance and the zero-phonon line E_2 as revealed by the absorption spectra taken from GaAs : EL2 single crystals.

3.3 STARK-EFFECT SPECTROSCOPIC DATA ON THE EL2 CENTER IN GaAs. — Time dependences of photocapacitance quenching in GaAs : EL2 for different values of anisotropic electric field are presented in figure 7. It can be seen that the direction of the field can either promote or oppose transition of the EL2 center to the metastable state, cf. $\mathcal{E} \| [111]$ and $\mathcal{E} \| [\bar{1}1\bar{1}]$ in the figure. In the first case, the effect of the increasing field is to accelerate the photocapacitance quenching process, while in the second, it is to quickly suppress the metastability properties of the EL2 center. This means that the Stark-effect spectroscopy data corroborate those of piezospectroscopy in identifying the EL2 center as a defect with C_{3V} symmetry. There is also evidence of good agreement with piezocapacitance spectroscopic data [12] and the results of DLTS studies using anisotropic electric field [14].

The kinetical studies of GaAs : EL2 photocapacitance, carried out for different wavelengths of the pumping light, have allowed determination of the spectral dependences describing the cross section for transition of the EL2 center to the metastable state, figure 8. Anisotropic influence of the electric field on the photocapacitance spectra bears evidence of a link that exists between the metastability mechanism and the EL2 center's symmetry. In its dynamical aspects, the metastability transition occurring under applied external field fits closely, with appropriate allowance made for the linear and quadratic Stark effect [17], the above-describe model (Fig. 3) of a tunneling deep defect. In order to provide a visual demonstration of the Stark shifts experienced by the defect's charge states along the different crystallographic axes, it is convenient to present, figure 9, the charge exchange on the EL2 center in a three-dimensional diagram of adiabatic potentials, where configurational axes Q_1, Q_2 and Q_3 pairs of the center's charge states, previously shown in figure 5. At $\mathcal{E} = 0$, $Q_1 \| [111]$, $Q_2 \| [100]$, $Q_3 \| [\bar{1}1\bar{1}]$; Q_1'' denotes the distance between the lattice site and the tetrahedral interstice, whereas $Q_2'' + \delta Q$ is the distance separating the site from the hexagonal interstice ; the distance shown in c' of figure 9 is that between the two types of interstices illustrated in figure 3. At $\mathcal{E} \neq 0$, $Q_1 \| [111] \cos(\mathcal{E}\,[111])$; $Q_2 \| [100] \cos(\mathcal{E}\,[100])$; and $Q_3 \| [\bar{1}1\bar{1}] \cos(\mathcal{E}\,[\bar{1}1\bar{1}])$ [17, 18]. The amount of the Stark shift for the D^+ and

D^{++} states also depends on the direction of the applied electric field : $D^{+} \Rightarrow \delta Q' = \frac{\delta F'}{\mathcal{K}}$; $D^{++} \Rightarrow \delta Q'' = \frac{2\,\delta F'}{\mathcal{K}}$ where $\mathcal{K}$ is the force constant and δF is the correspondingly changed electron vibrational constant ; $\delta F' = e\mathcal{E}\cos$ ($\mathcal{E} \parallel [110]$) ; $F'' = e\mathcal{E}\cos$ ($\mathcal{E} \parallel [100]$) [17, 18].

At zero electric field, energies E_2 and E_1 (Fig. 9) must correspond completely with the intervalley splittings $\Delta_{L\Gamma}$ and $\Delta_{X\Gamma}$. E_2 fully satisfies this requirement, but E_1, which is equal to 1.18 eV, is somewhat smaller than $\Delta_{X\Gamma}$. In the framework of the tunneling deep defect model, this discrepancy is accounted for by the Stark shift of the D^{++}-center along the [100] axis (see Fig. 3). As a possible source of the Stark shifts one can think of compensating acceptors [22, 23] which occupy positions in the arsenic sublattice along the [100] axis relative to the EL2 center. The Stark shifts that occur on application of anisotropic external electric field in the positions of adiabatic potentials describing the charge states of the EL2 center (Fig. 9) are consistent with the behavior of the corresponding spectra of photocapacitance quenching (Fig. 8). Indeed, the enhancement of quenching with increasing strength of the electric field applied along the [111] axis is seen in figure 8a to be accompanied by a slight broadening of the corresponding spectral line. The field dependence exhibited by the probability of the EL2 center to transit to the metastable state is manifestation of a greater probability that exists for two electron capture [17] (Fig. 9a) and momentum gained by Auger processes (Fig. 9b) in the presence of $\mathcal{E} \parallel [111]$. A slight shift observed in the position of the photocapacitance quenching peak is probably due to a decrease in E_2 energy which is a factor, albeit an indirect one, in the shaping of the optical self-compensation spectral dependence. An exactly opposite behavior of the photocapacitance quenching spectra is obtained with $\mathcal{E} \parallel [\bar{1}1\bar{1}]$, figure 8b. What is now observed is a drastically reduced probability for both two-electron capture (Fig. 9a) and Auger recombination of nonequilibrium carriers (Fig. 9b). The field-dependent shift in the position of the quenching peak toward lower energies, seen in figure 8b, is most likely due to a corresponding drop in the E_1 energy (Figs. 9a and b). The other two cases, viz. $\mathcal{E} \parallel [100]$ and $\mathcal{E} \parallel [110]$ (Figs. 8c and d), can serve as a good illustration of the nonmonotonic dynamics which characterizes the dependence of the changes in the probabilities for the above processes associated with the transition of the EL2 center to the metastable state upon the magnitude of the corresponding Stark shifts.

Thus, Stark-effect measurements performed on GaAs : EL2 samples placed in anisotropic electric field have confirmed the C_{3V} symmetry for the $EL2^0$ center and supported the assignment of the D^0, D^+ and D^{++} states to the L, Γ, and X valleys of the conduction band, respectively. The measurements also showed that anisotropic electric field is a controlling factor in recombination of nonequilibrium carriers and optical self-compensation of the EL2 center, the two processes which are accompanied by tinneling of the center's antisite component in the lattice of GaAs.

Summary.

Photo-EPR, pizospectroscopic and Stark-effect capacitance data have yielded identification of the EL2 center in GaAs as a double donor with C_{3V} symmetry ($EL2 = As_{Ga} + As_iV_{As}$), whose neutral, singly and doubly charged states form, respectively, from the wavefunctions of the L, Γ, and X valleys of the conduction band. Recombination of nonequilibrium carriers in GaAs : EL2 and optical charge exchange on the EL2 center occur *via* tunneling of the center's antisite component (As_{Ga}) between the lattice site (D^+ state) and the tetrahedral (D^0 state) or hexagonal (D^{++} state) interstices.

The mechanism that produces metastability of the EL2 center has been identified as an optical analog of the negative-U reaction of the form : $2\,D^+ + h\nu\,(E_1) \rightarrow D^0 + D^{++}$, which

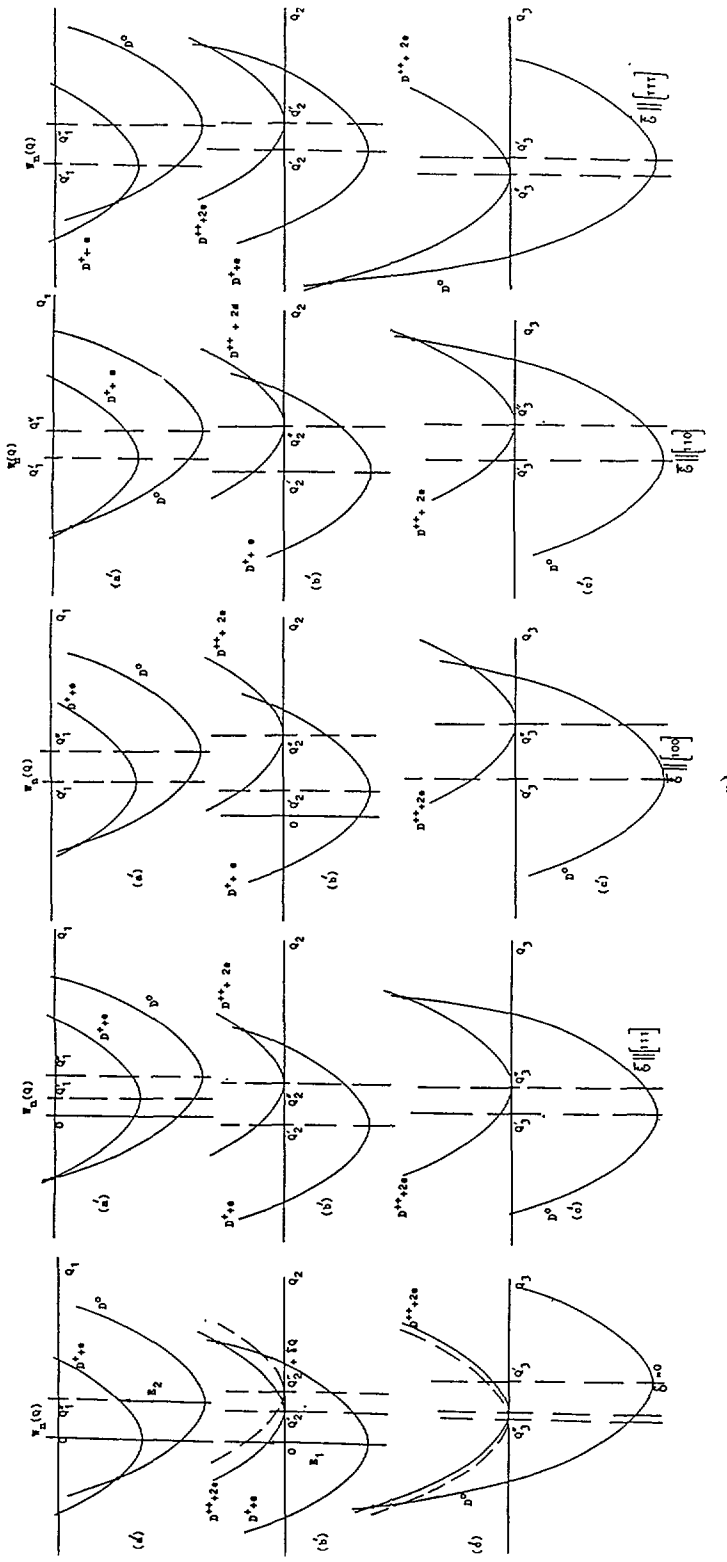
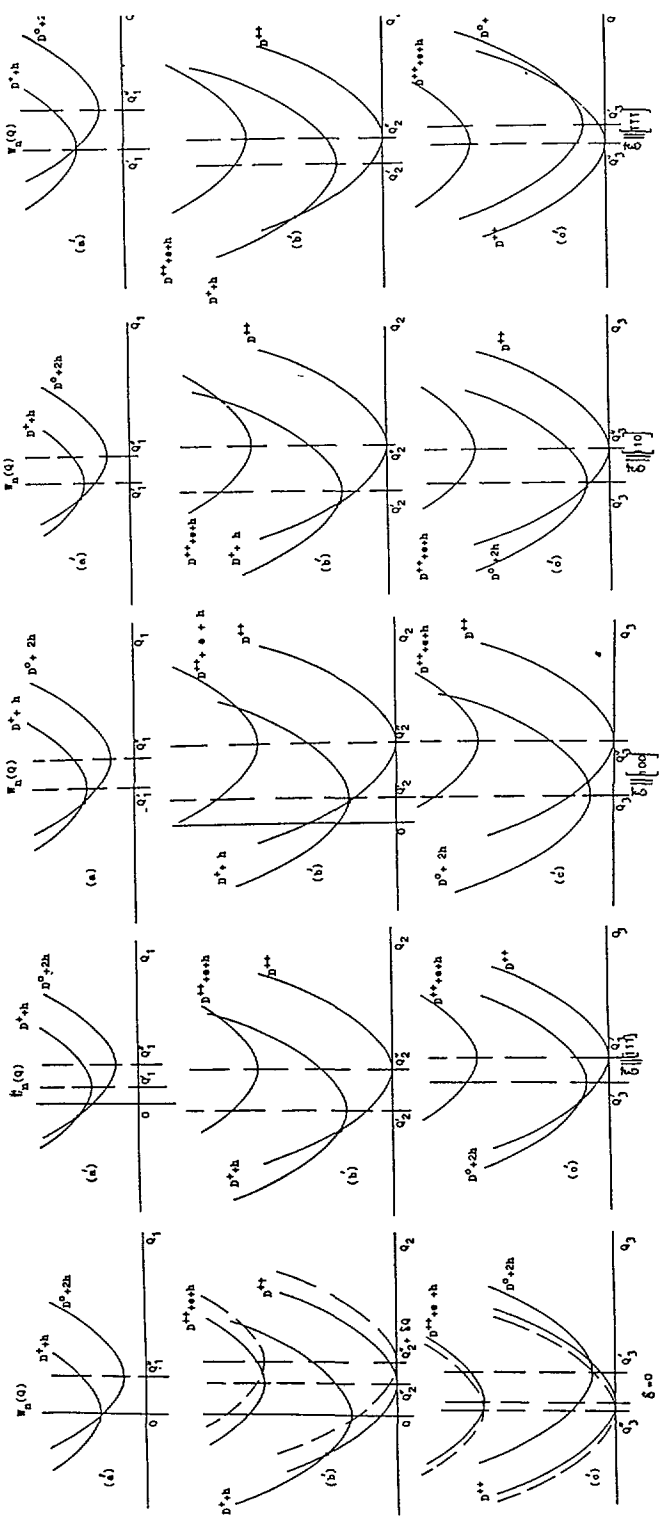


Fig. 9. — Adiabatic potentials for different charge states of the EL2 center in GaAs : (a) optical transition : defect to conduction band ; (b) optical transition : valence band to defect. The dash line ($\delta = 0$) shows the position of the adiabatic potentials describing the D^{++} state and corresponding to an antisite defect in the hexagonal interstice (see Fig. 3). The line also depicts the optimal conditions for the (+ / + +) transition to the X valley of the conduction band.



b)

Fig. 9 (*continued*).

gives rise to the tunneling of the antisite defect from the lattice site to the tetrahedral interstice. The two important consequences of EL2 metastability are enhanced quenching of $EL2^+$ EPR, and a drastic reduction of the nonequilibrium carrier lifetime. The latter consequence is manifested by quenching that affects interband photoconductivity, photocapacitance and the 1.039 eV zero-phonon line that is observed in GaAs : EL2 absorption spectra. Experiments on annealing the metastable neutral state of the EL2 center have shown that the temperature and rate of anneal are determined by the height of the energy barrier for the $D^0 + h \rightarrow D^+$ reaction. It was found that by varying the position of the Fermi level it was possible to control the degree of filling the interstitial arsenic atoms with electrons, and thus — through Auger recombination with its quenching effect — the intensity with which the EL2 center would display its metastable properties.

The possibility of control, over a wide range, has also been demonstrated for recombination of nonequilibrium carriers in GaAs — by controlling the probability for self-compensation of the EL2 center through the Stark shifts in the positions of its charge states, brought about by the anisotropic electric field applied to GaAs : EL2 single crystals.

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