Photoionization of the DX(Te) centers in $Al_xGa_{1-x}As$: Evidence for a negative-U character of the defect

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A detailed analysis of the photoionization of the DX(Te) centers in $Al_xGa_{1-x}As$ ($0.25 < x < 0.55$) has provided experimental evidence for the negative-U character of the defect. A variety of phenomenological models were considered but only the assumption that in ground state the DX center binds two electrons and forms a negative-U system allowed us to quantitatively describe the observed ionization kinetics at different temperatures and light intensities. The intermediate state of the process is not the effective-mass X- or Γ-like excited state of the DX center, but rather the neutral $(DX)^0$ state. This is strongly coupled to the lattice in the same way as the ground $(DX)^-$ state.

I. INTRODUCTION

Doping of GaAs or $Al_xGa_{1-x}As$ with Si, Sn, or group-VI elements produces defect states that behave as conventional shallow donors in GaAs or $Al_xGa_{1-x}As$ ($x < 0.2$). If the Al content in the alloy becomes larger, or alternatively high hydrostatic pressure is applied to GaAs or $Al_xGa_{1-x}As$ with lower x, new defect states that are still directly related to the chemical dopants control the carrier concentration. They are known as the DX centers.[1] In contrast to conventional donors, these states, while empty at low temperatures, do not recapture carriers. At low temperature the carriers either stay practically indefinitely in the conduction band (CB) or become metastably retrapped on the effective-mass-type excited states of the DX centers. The first type of behavior, known as persistent photoconductivity (PPC), is observed in the direct-gap $Al_xGa_{1-x}As$ alloys,[2] while the second is seen in the indirect-gap alloy. In the latter case the lowest conduction-band minimum becomes X-type and the effective-mass donor state associated with it is deep enough to capture photogenerated carriers without forming an impurity band.[3] Large lattice relaxation (LLR) around a defect, following electron capture by a DX state, is regarded as the most likely reason for metastability. The barrier preventing the electron from being captured originates from a strong electron-phonon coupling and exists only for a localized DX-type state.[4]

There is growing evidence that the DX-like phenomena are not just examples of curious behavior but can be expected to occur for many non-hydrogenic-like imperfections in a range of semiconductors. Normally the name of the center is reserved for donor-related defects in $Al_xGa_{1-x}As$. However, DX-like behavior has already been observed for some other defects CdF_2:In,[5] extrinsic

InSb,[6] $Cd_{1-x}Zn_xTe$:Cl,[7] $GaAs_{1-x}P_x$,[8] $Al_xGa_{1-x}Sb$:S,[9] and GaSb:S.[10] In spite of the fact that these systems have surprisingly similar optical and electrical properties, the dramatic differences in crystal ionicities and chemical identities of the defects lead us to suppose that in each case the defect may have a different microscopic structure and different atom rearrangement producing the LLR effects.[11]

Early papers proposed that the DX center was a complex of a donor and an unknown defect, possibly an arsenic vacancy.[12] However, the now established recent understanding is that the center is formed by the donor itself (not a complex), since the DX and shallow donor coexist and the sum of their concentrations is equal to the doped impurity concentration independent of crystal alloy compositions. Far-infrared local mode absorption measurements performed on Si-doped GaAs revealed[13] that the donor impurity, after ionization, occupies a substitutional position in the lattice. Consequently, the observation of a one-to-one correspondence between the concentrations of shallow donors and DX centers in $Al_xGa_{1-x}As$ with indirect-band-gap alloy compositions[14] justified the rejection of the supposition that a complex of point defects in a stable configuration could be responsible for the DX center.

Earlier Langer,[11] and more recently Chadi and Chang[15,16] and Morgan,[17] proposed that a substitutional-interstitial defect reaction may be responsible for the large lattice relaxation phenomenon. The most essential finding of the Chadi and Chang calculations is that the defect must capture two electrons to form the DX state, and therefore the DX state should be negatively charged. In GaAs under hydrostatic pressure or $Al_xGa_{1-x}As$ (for $0.2 < x < 0.8$), where the DX state is the ground state of the defect, the system must have a negative electron

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correlation energy, U ($U < 0$).[18,19]

Defects in semiconductors may, in general, possess many charge states. In most cases placing an extra electron on a defect requires more energy due to the Coulomb repulsion between electrons. This added interaction energy is defined as U, which is often called the Hubbard correlation energy.[18] For almost all defects, U has a positive value. If an electron-phonon interaction stabilizes a two-electron state more strongly than a single-electron state, then a quantity that governs the sequence of the energy levels is the difference between pure Coulomb electron-electron repulsion and the stabilization energy resulting from the electron-phonon interaction (e.g., due to the Jahn-Teller distortion). Such an effective correlation energy U_{eff} may be negative. This means that a two-electron level D^- lies below a one-electron level D^0 and causes a spontaneous disproportionation of two of the single-electron states D^0 into a pair of states, of which one is empty, D^+, while the second is a negatively charged two-electron state, D^-. This means that the D^0 state is thermodynamically unstable and thus may be observed only under nonequilibrium conditions. In semiconductors there are very few defect systems, for which the negative-U phenomenon has been unambiguously proven. Classic examples are the isolated vacancy in silicon and the interstitial boron in silicon. For both defects the level inverted structure has been unequivocally detected (see Ref. 19 for details). It should be stressed here that the essence of the negative-U phenomenon is a strong electron-phonon interaction at the defect (large lattice relaxation). Therefore, if for a given defect U is shown to be negative, a strong defect-lattice vibronic coupling must be involved. Such a strong coupling is a well-known phenomenon for defects in solids, but its existence does not automatically mean a negative U, e.g., the DX centers in GaAs.

According to the notation of Chadi and Chang, d denotes the fourfold-coordinated (substitutional) configuration of the DX center, and DX denotes the relaxed (broken-bond) configuration. The symbol D is used only to indicate the charge state of the defect without implying the bond configuration. A donor impurity forming the DX-like state in GaAs or $Al_xGa_{1-x}As$ may have several different neutral charge states: d_h^0 (effective mass, hydrogenlike associated with different CB minima), d_1^0 (nonhydrogen, i.e., with a high-symmetry lattice relaxation localized state predicted by Toyozawa's model[20] and recently observed by Dmochowski, Wasilewski, and Stradling[21]), $(DX)^0$ (with Jahn-Teller-type lattice relaxation). If the DX center forms a negative-U system, none of the neutral states of the center can be thermodynamically stable (present at low temperatures).

The very interesting result presented by Chadi and Chang has been confirmed independently with one rather significant difference. Chadi and Chang found that the one-electron $(DX)^0$ relaxed state is highly unstable, while Dabrowski, Strehlow, and Scheffler[22] found this state not only at lower energies but also suggest a possibility of a small barrier for its decay to a substitutional-type hydrogenic state. It is worth pointing out that the site instability proposed by Chadi and Chang seems to be a more gen-

eral property of the sp^3-bonded lattice, as the $sp^3 \rightarrow sp^2$ bond switching seems to be responsible also for a metastability of the $EL2$ defects in GaAs (Refs. 16 and 23) as well a passivation of donors and acceptors by H in Si.[24]

There is some experimental evidence to help in the identification of the DX centers with a two-electron negative-U system. The lack of paramagnetism of the ground state[25] and the lack of the electron-spin-resonance (ESR) spectrum even for a very high magnetic field[26] is most likely caused by a spin pairing effect for two electrons bound to the center. It was also observed that a high magnetic field decreases the electron capture rate,[27,28] presumably due to parallel spin polarization of the conduction-band electrons and electrons already bound to the defect in the neutral charge state. There is also an unexpected behavior of the electron mobility after photoexcitation,[3] and a surprisingly large hole capture cross section for the ground state.[29] Moreover, a single activation energy in the temperature dependence of the carrier concentration indicates the self-compensation effect[30] and acceptor character of the DX-center ground state. These facts, and some others of minor importance, although hardly explicable within the framework of a one-electron model of DX, can easily be interpreted using the two-electron, negative-U model of the defect.

For a defect forming a negative-U system, the neutral D^0 state (which is not being observed in thermodynamic equilibrium conditions) must play a crucial role in carrier capture and emission processes as an intermediate state $(D^- \leftrightarrows D^0 + e^- \leftrightarrows D^+ + 2e^-)$.[27,31] The aim of this study is to provide direct proof that the photoionization and capture processes for DX are indeed two-step processes, and moreover, that the defect forms a negative-U system. The agreement of the presented experimental data with a negative-U model of DX cannot be regarded as a proof of the model without a detailed examination of the other possible hypotheses. Different models of the defect were also used to quantitatively describe the observed processes, but only the assumption that the DX defect forms a negative-U system gives satisfactory fit to all experimental data. The intermediate state of the photoionization process is not the effective-mass X- or Γ-like excited state of the DX center, but a neutral $(DX)^0$, a not necessarily (but possibly) resonant state strongly coupled to the lattice, similarly to the ground $(DX)^-$ state.

II. EXPERIMENT

A. Samples and experimental details

In this study we have analyzed the temperature (40–130 K) and light intensity evolution of the photoionization process of the DX centers in $Al_xGa_{1-x}As$:Te. The samples used in the experiments were grown by liquid phase epitaxy on n-type Te-doped GaAs substrates with a net electron concentration $n > 10^{19}$ cm^{-3} ($\langle 100 \rangle$ surface plane orientation). The samples consisted of an

approximately 3-μm n-type Al$_x$Ga$_{1-x}$As $(0.25 < x < 0.55)$ layer doped with $(1-2) \times 10^{17}$ cm^{-3} Te and a subsequent 4-μm p^+-type layer of GaAs doped with about 10^{19} cm^{-3} Ge. The structure forms an asymmetric p-n junction with a depletion region (approximately 0.2 μm thick) in the Al$_x$Ga$_{1-x}$As layer. The composition parameter x of the Al$_x$Ga$_{1-x}$As layer was determined from photoluminescence or electron-microprobe measurements after removing the top p^+-type layer. Ohmic contacts were prepared as usual from Au-Ge and Au-Cr alloys for n-type and p^+-type crystals, respectively. The deep-level transient spectroscopy (DLTS) spectra of the samples showed only one dominant peak related to the *DX*(Te) center.

The samples were placed in a continuous-flow cryostat. A temperature controller enabled us to stabilize the sample temperature better than 0.2 K. A halogen lamp with a high-throughput prism monochromator was used as a source of a monochromatic light. The photon flux was varied using calibrated neutral density filters. The initial conditions for each of the transients were reestablished by heating the sample up to 140 K, and then cooling down to the temperature at which the process was investigated. Observed time constants varied typically from 0.2 to 1000 s. A recording system controlled by a computer allowed us to record transients with a data sampling rate up to 30 samples per second and with a dynamic of four and one-half orders of magnitude in amplitude.

The capacitance of the samples measured as a function of temperature (C-T curve) exhibits a large step at around 100 K. This step is not due to any change within the space-charge region of the diode but represents a substantial increase of the diode series resistance caused by the freeze-out of conducting electrons on the ground states of *DX* centers in Al$_x$Ga$_{1-x}$As, which are outside the space-charge region. For thin buffer layers (less than 0.5 μm) there are attempts to interpret such a drop of capacitance as being due to recapture of electrons at the edge of the space-charge region.[32] However, in thicker Al$_x$Ga$_{1-x}$As layers, as it is in our case, the effect of the increase of the series resistance must be much more pronounced. This effect makes standard experimental techniques, i.e., DLTS and C-V measurements, based on diode depletion region capacitance analysis applicable for the *DX* centers only at higher temperatures. Usually, photocapacitance measurements are performed at low temperatures to exclude a possibility of the thermal emission of the electrons from the defect. For the case of the *DX* centers the necessity of achieving slow thermal emission in the space-charge region implies also freezing out of all electrons in the bulk Al$_x$Ga$_{1-x}$As, and thus making this technique inapplicable for these defects. In many photocapacitance experiments performed on the *DX* centers apparent changes in the diode capacitance after sample illumination are nothing but a photogeneration of electrons in the Al$_x$Ga$_{1-x}$As outside the depletion region, and consequently, the decrease of the diode series resistance. These capacitance changes when properly transformed can be easily used for the observation of the true Al$_x$Ga$_{1-x}$As layer conductivity (see Appendix A for a detailed discussion).

B. Results

1. Rate equations and photoionization transients analysis

All of the photoconductivity transients were found[31] to be strongly nonexponential. At lower temperatures and for high light intensities they could be successfully modeled by two monoexponential functions (see note on Fig. 1 in Ref. 31) with the ratio of the two exponential components strongly depending on temperature and light intensity. The most extreme case of nonexponential behavior can be observed at higher temperatures and at relatively high photon fluxes, when the kinetics exhibits "overshoots" [Fig. 1(c)].

A variety of phenomenological models (e.g., two different donors with the strong compensation due to native or unintentional acceptors, one double donor, and a singly charged center with a long-lived excited state) have been considered in order to explain the data presented in Fig. 1 (see Appendix B for a detailed discussion). For some of these models an acceptable fit could be obtained for each individual kinetics but only the assumption that the two energy states of *DX* correspond to the two charge states of the negative-U-type defect provides a consistent explanation of all photoionization transients when the photon flux Φ was varied by up to three orders of magnitude.

The photoionization, thermal ionization, and electron capture kinetics for the defect can be derived from a set of rate equations describing carrier exchange between a two-electron defect and the conduction band. For such a defect the electron concentration n equals

$$n = N_D - N_A - N_1 - 2N_2 \tag{1}$$

and the rate equations are

$$dN_1/dt = -e_1 N_1 + e_2 N_2 + c_1(N_D - N_1 - N_2) - c_2 N_1 , \tag{2a}$$

$$dN_2/dt = -e_2 N_2 + c_2 N_1 , \tag{2b}$$

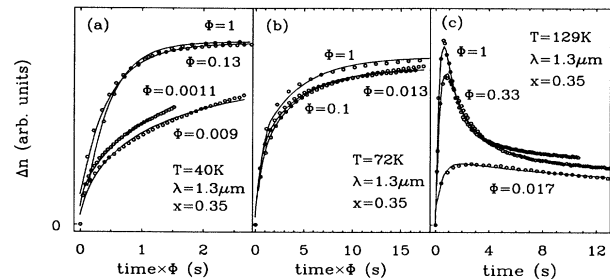where N_1 and N_2 denote the concentration of defects

FIG. 1. Photoionization transients for *DX*(Te) in Al$_{0.35}$Ga$_{0.65}$As for different photon fluxes (Φ) and at different temperatures. The lines are fits to the data according to the rate equations (1) and (2) with initial conditions for a defect forming a negative-U center. For any given temperature the fitting was done for all photon fluxes simultaneously. Note the different time scales for (a), (b), and (c).

possessing 1 and 2 electrons, respectively. The emission rates e_1 and e_2 are the sums of the thermal (e_t) and optical emission rates $(e_o = \sigma_o \Phi$, where σ_o is the photoionization cross section and Φ is the photon flux). The proportionality of the capture rates $c_{1,2}$ to the electron concentration may result in nonlinearity of these equations. When the capture rates $c_{1,2}$ are very slow (Appendix C) or the number of electrons participating in the process is only a fraction of all electrons in the crystal (e.g., in the isothermal DLTS measurements),[33] then these equations stay linear and can be solved analytically (Appendix C). Solution of this set of equations depends critically on the initial conditions and, therefore, on the sign of U, as well as on the type of experiment being performed, i.e., photoconductivity transients, isothermal DLTS (thermalemission process), or the electron-capture process.

The photoionization process should be studied at relatively low temperatures, where it can be assumed that $e_{t1,2} = 0$. If this condition is not fulfilled, then at low photon fluxes the thermal emission will contribute to the total ionization process making quantitative analysis of the photoionization less straightforward. Moreover, at higher temperatures it is not possible to achieve a complete freeze-out of all electrons on the center and the initial conditions for the process are temperature dependent.

If the sample is slowly cooled in darkness all of the electrons freeze-out on the defects. According to equilibrium statistics for the positive- and negative-U defects, the initial conditions depend on the sign of U in the following way:

$$N_1 = [D^0] = 0 \quad \text{and} \quad N_2 = [D^-] = \tfrac{1}{2}(N_D - N_A) \quad \text{for } U < 0 ,$$
(3a)

$$N_1 = N_D - N_A \quad \text{and} \quad N_2 = 0 \quad \text{for } U > 0 .$$
(3b)

In the photoconductivity experiment the photoexcited electrons modify the bulk conductivity, and thus the capture rates $c_{1,2}$ are not constant. During the fitting procedure these parameters can be redefined to make them independent of the electron concentration: $c_i = C_i n / N_D$ $(i = 1,2)$ and furthermore the C_i parameter be used as a constant.

Figure 2 shows a schematic diagram illustrating transitions of electrons between two charge states of a negative-U defect and the conduction band. The photo-

ionization kinetics derived from the rate equations (1) and (2) with the initial conditions for a negative-U defect [Eq. 3(a)] perfectly describe the photoionization transients at temperatures where the DX center is metastable (40 and 72 K) as well as at higher temperature (129 K) where it is not and the "overshoots" behavior is observed. For each temperature the transients for all photon fluxes were fitted simultaneously and only for the negative-U model of DX were all fitting parameters, i.e., the capture rates $C_{1,2}$ and photoionization cross sections $\sigma_{01,2}$, independent of the light intensity. The lines in Fig. 1 represent the fits to the experimental data.

Table I summarizes the fitting parameters obtained for data shown in Fig. 1. It is seen that the capture rate C_1 strongly depends on temperature and vanishes for $T < 72$K, which represents the inability of the empty DX center $(D^+$ charge state) to recapture the first electron at low temperatures. An increase of C_1 between 72 and 129 K reflects exactly an activation character of the electron-capture cross section already found for Te-related DX centers in $Al_xGa_{1-x}As$.[34] Interestingly, the capture rate C_2, i.e., the capture rate of the second electron by the DX center in the neutral charge state D^0, depends very weakly on temperature and even for $T = 40$ K it is close to 1 s^{-1}, which means that even in the PPC regime the photogenerated D^0 state efficiently captures the second electron. The electron-capture cross section for the $D^0 + e^- \rightarrow D^-$ process derived from the values of the parameter C_2 is very small when compared to that for the normal deep donor states.[35] It confirms again that the initial state of the DX center for this process has no long-range Coulomb potential, but it does not necessarily mean that there is a vibronic energy barrier between the $(DX)^-$ and $(DX)^0$ states of the defect. The large (and weakly temperature dependent) electron-capture rate C_2 indicates also that the capture of the second electron occurs while the DX center is already in the relaxed state.

The most surprising finding was that the emission rate e_1 of the neutral $(DX)^0$ state was dominated for lower temperatures (and all illumination conditions) by the photoionization process. This may not be the case for the higher temperature of 129 K where the fitting procedure was very weakly dependent on the parameter e_1. At this temperature one can expect that the D^0 charge state of DX is already partially occupied, and thus, the thermalemission rate e_{t1} can dominate. This result indicates the existence of a relatively high barrier for the thermal ionization of this state, which is obviously not the case of the hydrogenlike, excited, effective-mass states of the DX centers.
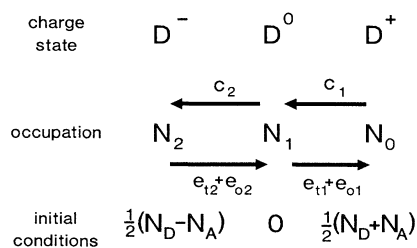

FIG. 2. Diagram illustrating the rate equations (1) and (2) for a defect having two charge states and initial conditions (3a) for its photoionization process.

TABLE I. Fitting parameters obtained for photoionization of the DX(Te) in $Al_{0.35}Ga_{0.65}As$ (Fig. 1).

Initial state	T (K)	40	72	129
$(DX)^-$	e_{o2}	2.6	0.63	0.54
$(DX)^0$	e_{o1}	21	6.1	
$(DX)^0$	c_2	1.2	2.9	11
$(DX)^+$	c_1	$< 10^{-4}$	0.0013	3.8

2. Photoionization cross-section analysis for (D X)⁻ and (D X)⁰

The spectral dependencies of the low-temperature photoionization cross sections of the $(DX)^-$ (σ_{o2}) and $(DX)^0$ (σ_{o1}) states for $Al_xGa_{1-x}As$ alloys with $x = 0.25$, 0.35, 0.45, and 0.55 are shown in Fig. 3. The spectral shape and energy position of the photoionization cross section σ_{o2} of the ground $(DX)^-$ state is the same as determined in many previous experiments[12] (see the discussion of a widely used initial slope method given in Appendix C). There is a very small shift in energy between the spectra corresponding to different crystal compositions, indicating a weak dependence of the electron ionization energy of the $(DX)^-$ center on the alloy composition. A similar conclusion has already been reached from a study of the *DX*(Te) (Ref. 12) and *DX*(Si) (Ref. 36) centers. This indicates also that the Gaussian low-energy tail of the spectrum cannot be due to the broadening caused by alloy fluctuations. Flattening of the spectrum with increasing temperature suggests phonon broadening [Fig. 4(b)]. Such broadening is expected to occur if the large lattice relaxation (LLR) model of the center is valid.

While the spectral shape and energy position of the photoionization cross section σ_{o2} is almost unchanged for all crystal compositions considered, there is a distinct change in the shape of σ_{o1} [neutral $(DX)^0$ state] as well as in its relative position with respect to σ_{o2} for different alloy compositions. The behavior of the photoionization cross section σ_{o1} has all the characteristic features of a center with a strong electron-phonon coupling [Fig. 4(a)] and, especially for higher mole fractions of aluminum content, is quite similar to σ_{o2}. In the direct-band-gap
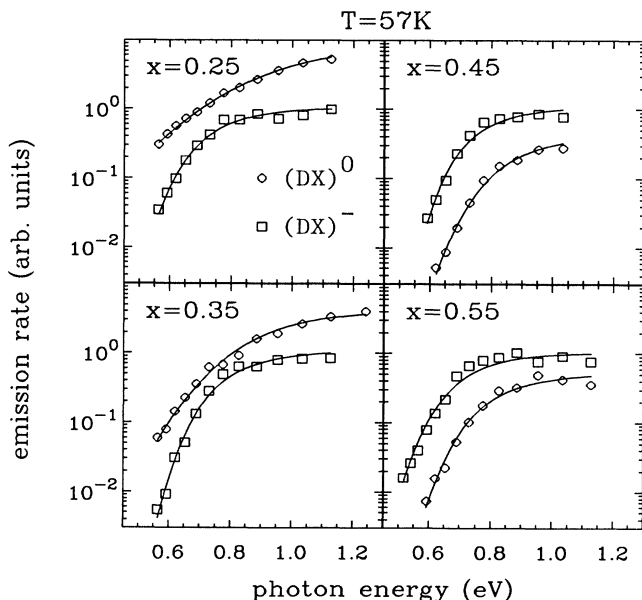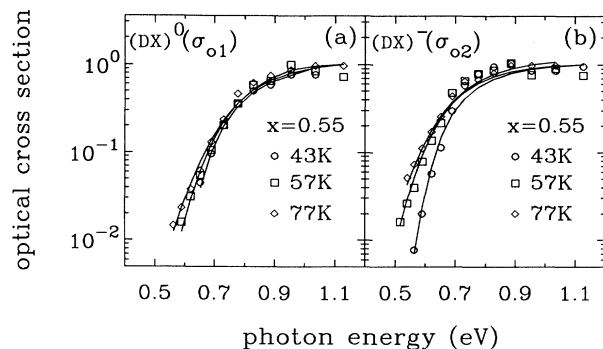

FIG. 4. Photoionization cross sections for one-electron $(DX)^0$ (σ_{o1}) and two-electron $(DX)^-$ (σ_{o2}) energy states of the *DX* center in $Al_{0.55}Ga_{0.45}As$ at different temperatures.

range of the alloy compositions, the photoionization of the *DX* center in the neutral D^0 charge state is almost an order of magnitude more probable than that for D^- (see Fig. 3). For crystals with an indirect band gap this sequence is reversed. At lower temperatures for the sample with $x = 0.35$ and for low photon energies these two probabilities were found to be very similar, however the very intensive electron-recapture process for the D^0 state makes the effective photoionization of D^- very slow. A slope of σ_{o1} for low photon energies decreases with temperature suggesting again that the photoionization of the *DX* center in the neutral charge state is associated with a multiphonon process [Fig. 4(a)].

The photoionization cross sections of the *DX* center in both charge states were quantitatively analyzed using the model of the process for a localized defect strongly coupled to the lattice vibrations[3,37] (see Appendix D). In this model the slowly varying part of the photoionization cross section (high photon energies) is mainly governed by the electronic part of the defect wave function. Transitions for very low photon energies (lower than the photoionization threshold E_{opt}) are only possible due to a very strong electron-phonon interaction. The strength of this interaction is described by the broadening parameter (E_b), being very sensitive to the value of the relaxation energy $E_{opt} - E_{th}$, and temperature [see Eq. (D3) in Appendix D].

Table II summarizes the values of the photoionization threshold and the broadening obtained from the fitting procedure of the photoionization rates observed in the experiment to the model described in Appendix D. The high quality of the fit, as well as the temperature trends in the broadening parameters, strongly support the validity of the model of the process. To get reliable values of both energies, it is necessary to know the optical cross section in the widest possible range of its values. Unfortunately, observation of the process is in conditions where very effective electron recapture occurs, making measurements of the very slow emission rates extremely inefficient. For this reason, in the samples with the low aluminum content, where the electron recapture for D^0 was found to be very fast, the values of the cross section for the D^0 charge

FIG. 3. Photionization cross sections for one-electron $(DX)^0$ (σ_{o1}) (circles) and two-electron $(DX)^-$ (σ_{o2}) (squares) energy states of the *DX* center at 57 K.

TABLE II. Photoionization threshold and broadening parameters obtained according to the model presented in Appendix D.

(a)

$x = 0.25$	$(DX)^0$ (σ_{o1})		$(DX)^-$ (σ_{o2})	
T (K)	E_{opt} (eV)	E_b (eV)	E_{opt} (eV)	E_b (eV)
57	0.80	0.27	0.61	0.089
69	0.80	0.30	0.59	0.105

(b)

$x = 0.35$	$(DX)^0$ (σ_{o1})		$(DX)^-$ (σ_{o2})	
T (K)	E_{opt} (eV)	E_b (eV)	E_{opt} (eV)	E_b (eV)
40	0.75	0.16	0.65	0.092
48	0.78	0.17	0.62	0.082
57	0.75	0.18	0.66	0.084
84	0.78	0.24	0.57	0.083

(c)

$x = 0.45$	$(DX)^0$ (σ_{o1})		$(DX)^-$ (σ_{o2})	
T (K)	E_{opt} (eV)	E_b (eV)	E_{opt} (eV)	E_b (eV)
32	0.73	0.11	0.65	0.072
43	0.74	0.11	0.63	0.066
57	0.72	0.11	0.63	0.074
84	0.70	0.14	0.59	0.092

(d)

$x = 0.55$	$(DX)^0$ (σ_{o1})		$(DX)^-$ (σ_{o2})	
T (K)	E_{opt} (eV)	E_b (eV)	E_{opt} (eV)	E_b (eV)
43	0.69	0.078	0.61	0.057
51	0.68	0.081	0.59	0.070
57	0.66	0.094	0.59	0.090
68	0.69	0.107	0.62	0.10
77	0.69	0.124	0.60	0.11

FIG. 5. Configuration coordinate diagram for DX(Te) in $Al_{0.35}Ga_{0.65}As$ illustrating all transitions possible for the defect and constructed using the data presented in Table I.

states cannot be observed for very low photon energies. Despite this, the model also gives in this case very-well-defined values of parameters, but they are of less importance than those for the higher aluminum content.

III. DISCUSSION AND CONCLUSIONS

Figure 5 shows the configuration coordinate diagram of DX(Te) in $Al_{0.35}Ga_{0.65}As$ constructed on the basis of the transition rates summarized in Table I and the parameters extracted from the spectral dependencies of the photoionization cross sections (Table II). According to the model of Chadi and Chang, the lattice configuration (bond structure) of DX in the D^+ and D^- charge states are different. Thus, the local phonon modes, which are coupled to the defect in both charge states, are also not the same. This means that these vibrations have to be described by a different configuration coordinate. The use of a one-dimensional diagram for three charge states of a defect, where additionally local lattice rearrangement occurs, will always be a simplified description of possible ionization and capture processes. If the interstitial-substitutional defect motion is involved in the DX-center ground-state formation, it means the one of the ioniza-
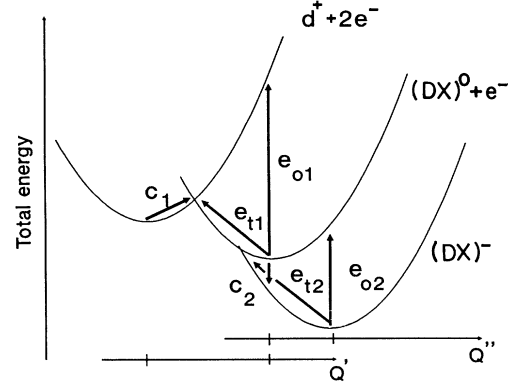
tion (capture) processes is accompanied by motion of the defect, not only in the Q space of the configuration coordinate, but in the real space as well. From the observation of the photoionization processes we conclude that this lattice reorganization happens when the second ionization process $(D^0 \rightarrow D^+ + e^-)$ occurs. Thus, there is no real transition: $(DX)^0 + e^- \rightarrow d^+ + 2e^-$, but it should be written in the following way: $(DX)^0 + e^- + h\nu \rightarrow (DX)^+ + 2e^- \rightarrow d^+ + 2e^-$. This process transfers only one electron to the CB and so cannot be resolved into two separate processes by our experimental procedure. The true energy barrier responsible for the metastability of DX is not vibronic, as it is depicted in Fig. 5 between $(DX)^0 + e^-$ and $d^+ + 2e^-$ states, but an ionic, and consequently two-dimensional configuration coordinate diagram similar to that suggested in Refs. 11 and 37, is much more appropriate. However, in order to better visualize two-step ionization and capture processes for the DX center, it is much more convenient to use the diagram in the simple form presented in Fig. 5, where a change of the local phonon mode and the lattice reconfiguration during $D^- \leftrightarrows D^0$ and $D^0 \leftrightarrows D^+$ transitions are represented by the use of two different configuration coordinates Q' and Q''.

In the analysis of the photoionization transients using rate equations it was assumed that no other short-lived energy states of the DX center participate in these processes. A limiting experimental factor was the sampling rate (approximately 30 samples/s) of the apparatus making it impossible to record very fast processes. However, these states, if present, may very effectively participate in the processes of the electron exchange between DX and the CB, and definitely influence the spectral and temperature dependencies of the observed ionization and capture processes. Thus, the photoionization and capture parameters obtained from the presented analysis are valid no longer than the assumed scenario of the processes is correct. In this approach only two main processes are considered: $D^- \leftrightarrows D^0$ and $D^0 \leftrightarrows D^+$. If these processes are more complicated than simple ionization and

electron-capture processes, then the parameters we obtained must contain some information about this fact. For instance, any intracenter defect transformation (reconfiguration of a bond structure) that does not result in the appearance of an electron in the conduction band will not be seen in the type of experiment discussed here. On the other hand, this process will definitely have an influence on the values of the parameters obtained.

The photoionization process is a momentum conserving process (vertical in k space), but it is also a configuration-conserving process according to the adiabatic approximation for the lattice vibrations (vertical in Q space). According to the experimental data, the first process in the DX-center ionization is $(DX)^- \rightarrow (DX)^{*0} + e^-$. The final state of the photoionization must be the $(DX)^{*0}$ state, i.e., a highly vibrational excited state of $(DX)^0$ (Fig. 5). Next, the defect emits phonons and relaxes to $(DX)^0$ [$(DX)^{*0} \rightarrow DX^0 + \text{phonons}$]. This process is very fast, comparable with a period of lattice vibrations ($\sim 10^{-13}$ s). In Ref. 16 it is proposed that this defect spontaneously transforms to fourfold coordination [$(DX)^0 \rightarrow d^0 + \text{phonons}$], and then, because d^0 is unstable, loses the second electron: $d^0 \rightarrow d^+ + e^-$. The latter two reactions are also very fast. If the photoionization proceeds as suggested in Ref. 16, the second photoionization process would not be observed. In our experiments we do observe this process, so we propose the following. The DX center in the (DX^0) configuration is unstable. It may transform to d^0 and then emit the electron (these two processes constitute a simple thermal-emission process). The reaction $(DX)^0 \rightarrow d^0$ must be accompanied by the bond reconstruction, and thus it needs to overcome the ionic energy barrier,[11,37] making this process highly unlikely at low temperatures. This is because the same energy barrier denying the reverse reaction is responsible for the metastability effects in DX. Much more probable processes for $(DX)^0$ vanishing are the second photoionization $(DX)^0 + e^- + h\nu \rightarrow d^{*+} + 2e^- \rightarrow d^+ + 2e^- + \text{phonons}$, or the electron capture $(DX)^0 + e^- \rightarrow (DX)^{*-} \rightarrow (DX)^- + \text{phonons}$. Because it was found that the second reaction is very effective even at low temperatures, we concluded that the photoionization process must proceed as $(DX)^- + h\nu \rightarrow (DX)^{*0} + e^- \rightarrow (DX)^0 + e^- + \text{phonons}$, and then $(DX)^0 + e^- + h\nu \rightarrow d^{*+} + 2e^- \rightarrow d^+ + 2e^- + \text{phonons}$, and so the intermediate state of the process is $(DX)^0$, not d^0. During sample illumination there is a non-negligible amount of the DX defects in the $(DX)^0$ state [see Eq. (D1)]. If the light is turned off, when some of the centers are not photoionized, then the electron-capture process [i.e., $(DX)^0 + e^- \rightarrow (DX)^{*-} \rightarrow (DX)^- + \text{phonons}$, described by the parameter C_2] is the way the defect relaxes from the excited, unstable state $(DX)^0$ to the ground state $(DX)^-$.

The values of the photoionization threshold for $(DX)^0$ (σ_{o1} columns in Table II) are greater then for $(DX)^-$, but it does not necessarily mean that the $(DX)^0$ state is resonant with the conduction band. The certainty is that the second ionization process ($D^0 \rightarrow D^+$) is accompanied by a much more pronounced multiphonon emission that for the first ($D^- \rightarrow D^0$). It also means that the relaxation energy of the distorted lattice is larger for the first case than

it is for the latter. If the relaxation energy for the $D^0 \rightarrow D^+$ transition is greater than the energy needed to ionize the center, it will imply that the $(DX)^0$ state is probably resonant with the CB. The photoionization broadening parameter E_b for both photoionization processes of the defect increases with the temperature, indicating the phonon-assisted type of these processes (Fig. 4). The broadening parameter E_b of the threshold for the $D^0 \rightarrow D^+$ transition is greater than that for $D^- \rightarrow D^0$ at corresponding temperatures, suggesting again that the lattice distortion is large for the first process. However, it is not clear to what extent the change of the energy of the local phonon coupled to the defect in both charge states may influence the broadening. The energies of these phonons may have no relation with the energies of the phonons of the lattice, and it is very difficult to draw conclusions about the relaxation energy knowing only the broadening parameter E_b.

A direct participation of the effective-mass states of the DX centers could only be observed for the $D^+ \rightarrow D^0$ process, where the DX defect in the D^+ charge state has long-range Coulomb potential and such states are present. In this paper the $D^+ \rightarrow D^0$ process, being described by the parameter C_1, is negligibly slow at the temperatures where the spectral dependencies of both photoionization processes were studied, i.e., in the PPC regime. It also means that the analysis of the two-step capture process presented in Ref. 38 addresses mostly this $D^+ \rightarrow D^0$ transition, while in our experiments due to the low temperatures and photoionization rates observed, this transition can be practically disregarded. However, there is no reason to assume, *a priori*, that the intermediate states for the electron-capture process to the initially empty DX center ($D^+ \rightarrow D_c^0 \rightarrow D^-$) and the intermediate state $(DX)^0$ for the (photo)ionization processes of the initially filled DX defect ($D^- \rightarrow D_i^0 \rightarrow D^+$) are the same. Both processes are dynamic, and the filling and emptying of the defect by electrons, especially at higher temperatures, are an interplay between electron capture and emission by the defect in different charge states, as well as embracing the processes of bond reconfiguration.

There is a very important question regarding the role of the shallow hydrogenlike effective-mass states of the DX centers in the ionization and capture processes. For samples with the direct-band-gap alloy composition the concentration of impurities is far above the concentration where the Mott transition occurs, so these states are simply a part of the conduction band. In crystals with an indirect band gap, the X-like effective-mass states can be observed and they can very effectively reduce the concentration of electrons in the band, especially at lower temperatures.[3] However, due to the fact that they are in thermal equilibrium with the band, it is not possible to see them in the kinetics. The capture rates C_2 found in the crystals with an indirect band gap are lower than for the direct one. This effect can be nothing else but a manifestation of the X-like effective-mass states of the DX center.

In the above analysis it was assumed that there is no broadening effects of the parameters due to random-alloy fluctuations. The ionization and capture rates were re-

garded as average values characteristic for the whole crystal. However, it is necessary to remember that for the defect forming a negative-U system the capture and emission are two-step processes, so they are, in principle, nonexponential. This indirect way of changing the defect charge state is an intrinsic feature of the center and the fundamental reason for the observation of a nonexponential processes. When the negative-U defect is analyzed assuming a one-electron center, then the capture and ionization parameters must be interpreted as "broadened," i.e., the kinetics are not perfectly exponential. Numerous authors have analyzed the thermal emission of electrons from the DX center and found it to be strongly nonexponential. Usually, the random-alloy fluctuations were proposed as the reason for this phenomenon. On the other hand, this finding is in obvious contradiction with the widely observed independence of the thermal and optical ionization processes in relation to the crystal alloy composition. Such an ambiguity does not exist when the kinetics are analyzed using the model presented in the study.

The first step in the ionization process was found to be independent of the alloy composition. This process may be an intracenter transition (e.g., $1ss \rightarrow 1sp$) followed by the very fast autoionization of the $(DX)^-$ center to the $(DX)^0$ state. Another possibility is a thermally or optically driven defect reconfiguration, i.e., a transfer of the interstitial position atom to another interstitial position equivalent to the $\langle 111 \rangle$ direction. The lattice surrounding the defect after such a reconfiguration is in a highly excited vibrational state, so this may result in the release of the first electron. The intracenter transition can be almost independent of the crystal alloy composition. The dynamics of the defect reconfiguration process will be mainly governed by an ionic barrier formed by the first-nearest neighbors (arsenic atoms). In this case one can expect that the second-nearest neighbors (gallium or aluminum) are less important, so the influence of the alloy composition alloy on this process will not be very strong.

The first step in the ionization process may dominate the capacitance transients observed in the DLTS experiments (see Ref. 33 for details), while the second step $(D^0 \rightarrow D^+)$ may introduce only a distortion of the transients. Due to the mathematical and physical complexity of the problem, it is not possible to evaluate the magnitude of the real influence of the local alloy fluctuations on the defect parameters. This influence may manifest itself in different ways in different processes, depending on the localization of the initial and final state.[34] When the ionization and capture processes are analyzed in terms of the two-step processes, the interpretation of the broadening effects must be reconsidered.

IV. SUMMARY

A detailed analysis of the photoionization of the DX(Te) centers in $Al_xGa_{1-x}As$ ($0.25 < x < 0.55$) has revealed that the process goes through two steps: $(DX)^- + h\nu \rightarrow (DX)^0 + e^-$ and $(DX)^0 + h\nu \rightarrow d^+ + e^-$.

The intermediate state of the process is not the effective-mass X- or Γ-like excited state of the DX center, but the neutral $(DX)^0$ state, strongly coupled to the lattice, similar to the ground $(DX)^-$ state. Using rate equations with initial conditions characteristic of a defect forming a negative-U system, it has been possible qualitatively and quantitatively to describe the observed ionization kinetics for different temperatures and photon fluxes. No acceptable fit to the data was possible when rate equations and initial conditions are used that are characteristic of two different donors with strong compensation; one double donor or a single donor with a long-lived excited state were applied. This result provides conclusive experimental evidence for the model of the Chadi and Chang identifying the DX defect as a center forming a negative-U system.

The photoionization threshold for the first ionization process $[(DX)^- + h\nu \rightarrow (DX)^0 + e^-]$ was found to be independent of the alloy composition, however a decrease of the threshold energy for the second photoionization $[(DX)^0 + h\nu \rightarrow d^+ + e^-]$ with increasing aluminum content was observed. The DX center in the $(DX)^0$ state very effectively recaptures the electrons from the conduction band even at very low temperatures, making it impossible to observe this state under a condition of thermal equilibrium. When the second photoionization process occurs, the defect undergoes a bond reconfiguration process and due to an ionic energy barrier cannot capture electrons at low temperatures. Consequently, metastability effects for the defect are observed.

ACKNOWLEDGMENTS

APPENDIX A: RELATION BETWEEN MEASURED DIODE CAPACITANCE AND THE ELECTRON CONCENTRATION IN THE $Al_xGa_{1-x}As$ LAYER

An electrical equivalent circuit of the semiconductor layered structure used in the experiments consists of a constant capacitor formed by the junction depletion layer and a variable series resistor formed by the $Al_xGa_{1-x}As$ layer outside the junction. The measured capacitance of such a structure equals $C_m = C_0/(1 + \omega^2 C_0^2 R^2)$, where C_0 is the capacitance of the diode space-charge region, R is the diode series resistance, and ω is the angular frequency of the test signal used in the capacitance meter. Due to zero diode bias during all of the experiments and a small test signal of the capacitance meter, the leakage current is neglected. Assuming that the changes in the resistance R come mainly from changes in the electron concentration n in the $Al_xGa_{1-x}As$ layer,

$$n \approx (C_0/C_m - 1)^{-1/2} . \qquad (A1)$$

The validity of this approach was checked by fitting formula (A1) to the experimentally observed $C(T)$ dependence. Use of the equilibrium statistics for the electron concentration for the negative-U model of the center gave exactly the same value of $E_d = 0.06$ eV as for the direct Hall measurement on identical samples (same technology, same crystal composition and doping level[30]).

The most important argument for the validity of this approach comes from a direct observation in the structures of the freezing-out of electrons on X-like effective-mass ($x = 0.55$) states of the DX centers after the photo-ionization of the DX-center ground state at low temperatures ($T < 15$ K). If the DX defects causing the drop of capacitance discussed here had been in the space-charge region, then the electrons released from the defect during the photoionization process would have been immediately swept away by the electric field. Consequently, no recapture on the hydrogenic states of the DX center could occur. Moreover, at the high electric field present in the space-charge region, the Coulomb potential of the donor state does not form any bound states because of the very strong Poole-Frenkel effect. Thus, the observation of a low-temperature step on the $C(T)$ curve after photoionization of the DX center at low temperatures (dashed line in Fig. 6) confirms that the DX defects responsible for the drop of the capacitance at lower temperatures are in a *neutral* region of the $Al_xGa_{1-x}As$ layer.[39]

A very important question is the range of concentrations possible for observation using this method. Let α be a fractional change of C_0, possible to observe using the available apparatus

$$C_m < (1 - \alpha)C_0, \quad \alpha \to 0 . \qquad (A2)$$

Taking into account all diode parameters and relation (A2), we can evaluate the highest electron concentration that it is possible to observe: $n < 5 \times 10^{14}/\alpha^{1/2}$ cm^{-3} and $n < 10^{14}/\alpha^{1/2}$ cm^{-3} for crystals in the indirect- and
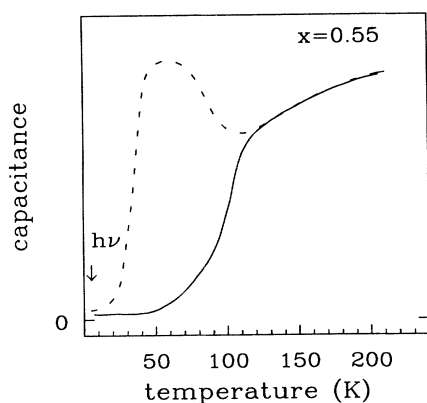

FIG. 6. Diode capacitance vs temperature curves (C-T). The dashed line is the C-T curve for heating after a brief illumination of the sample by monochromatic light at low temperature (see text).

direct-band-gap alloy compositions, respectively (the difference comes from different electron mobilities). Our measuring equipment allowed us to register the capacitance with an accuracy of $4\frac{1}{2}$ digits giving $\alpha = 10^{-4}$. The use of a 6-digit voltmeter with input dc compensation allows a decrease in α by several orders of magnitude. It is also possible to compensate a high-temperature diode capacitance (as it is done in the DLTS experiments) and measure the diode capacitance differentially at a much higher capacitance meter sensitivity. In practice, the limiting factor in this case is the signal-to-noise ratio, but when special care is taken, the value of $\alpha \cong 10^{-6}$ can be easily achieved, so reaching the highest concentrations considered.

The lower limit of the electron concentrations available is defined by the lowest sample capacitance it is possible to measure, i.e., the capacitance of cables equal ~ 1 pF. According to formula (A1), it translates to $n > 2 \times 10^{13}$ cm^{-3} and $n > 4 \times 10^{12}$ cm^{-3} for indirect- and direct-band-gap ranges of the alloy compositions, respectively.

When the sample is cooled down the occupancy of the defect is governed by equilibrium statistics only when the time necessary to reach this equilibrium is much less than the cooling time. It means that due to metastability effects associated with the DX centers during the cooling process some electrons always stay in the conduction band without any chance of being captured at temperatures where the PPC is observed. The rate equations presented in the paper are linear at the beginning of the photoionization process (in a sense nonlogarithmic) with respect to the values of the N_1 and N_2 parameters. Consequently, the initial conditions $n = 0$ for $t = 0$ are correct in the initial concentration of electrons, which is less than 1% of N_D. This small amount of electrons does not influence the quantitative analysis of the process.

APPENDIX B: OTHER HYPOTHESES CONSIDERED TO EXPLAIN THE EXPERIMENTAL DATA

Any possible model to be considered for qualitative analysis of the experimental data presented in this paper must explain two main features. First of all, it is obvious that either two centers or two energy states of the same center must participate in the photogeneration of carriers into the conduction band. These two states have to exhibit metastability, because the effect of persistent photoconductivity is observed. Secondly, one of the centers must be only partially occupied, or completely empty, in thermal equilibrium. This is a necessary condition for the observation of the overshoot behavior of the photoconductivity immediately after the sample is illuminated by light. In this case a large number of empty states very effectively recapture the photogenerated carriers and compete with the photoionization process.

Hypothesis 1: Two different donors. The DLTS spectra of the samples have only one peak attributed to the Te-related DX center. However, it is known that the DX centers related to group-VI donor dopants, i.e., Te, Se, and S, have DLTS peaks in exactly the same position.[40] The most probable unintentional impurity in liquid-phase-epitaxy-grown material is sulfur. Undoped sam-

ples grown by the same technology as those used in the experiments have a free-electron concentration at least one order of magnitude lower than the samples used in the study, which were intentionally doped with tellurium.[41] One of these two DX centers must be partially compensated by additional acceptors to form a large number of empty states for the recapture process at higher temperatures. This system is schematically shown in Fig. 7(a). The kinetics derived from rate equations similar to those presented in the text and in Appendix C enable some individual transients observed in the experiment to be successfully fitted, however to do this it was necessary for the ratio of concentrations of these two defects to vary with temperature and light intensity. Consequently, no acceptable fit was found where the transients from the same temperature and for different photon fluxes were analyzed simultaneously.

Hypothesis 2: One defect with an excited state of the same charge state. In this hypothesis the DX center has to have an excited state, which can be populated by light. The spectral dependence of this transition must be very broad and coincide with the spectral range applied in the experiments if effective population of the excited state is to occur. This state should also be long-lived and the recovery of the defect to the ground state should be slow (similar for the excited state of the $EL2$ defect in GaAs). These requirements imply a large difference in the lattice relaxation for the excited and ground states of the defect, however the LLR for the excited state must still be large. This is because the state cannot be filled by electrons from the conduction band in the temperature range where the metastability of DX is observed. Consequently this excited state of DX cannot be the hydrogenlike effective-mass state of DX. This system [see Fig. 7(b)] can also give a reasonable fit to the individual transient, however no acceptable quantitative description for different temperatures as well as for different photon fluxes exists. This system is also most unlikely to explain the overshoot behavior of the photoconductivity, because the defect can be either in the ground or excited state, and consequently there are no empty defects to recapture electrons from the conduction band. Only when unreasonably high compensation is assumed does this system exhibit overshoot behavior.
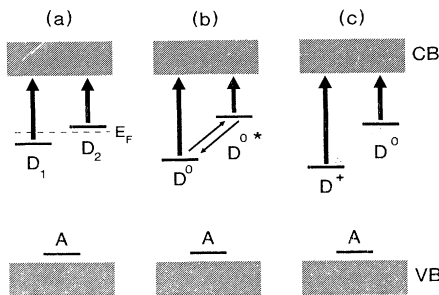

FIG. 7. Other hypotheses considered to explain the data: (a) a two-donor system, (b) one donor with long-lived excited state populated by light, and (c) a double donor (see text).

Hypothesis 3: Two charge states of a double donor. The DX centers in this model have three charge states: D^{2+}, D^+, and D^0 [see Fig. 7(c)]. Depending on the sign of the electron correlation energy (positive- or negative-U case), the higher-energy state is D^0 or D^+, respectively. The center must also be partially compensated by acceptors. For tellurium to form such a double-donor state, it need not necessarily be substitutional but could be in an interstitial position or form a defect complex. In this case, there is a chance that by forming a different bond structure, it may be possible to release two of its electrons and form a double-donor state. When it occupies the anion sublattice it is a simple single donor. Far-infrared absorption due to local vibration modes for Si in GaAs showed that indeed the silicon atom when ionized occupies a substitutional position in the arsenic sublattice and it is not accompanied by any other point defect.[13] Numerous similarities between DX centers related to silicon and tellurium allow us to conclude that the latter does not occupy an interstitial position, and consequently the formation by a tellurium atom of double-donor states is most unlikely. Beside the structural arguments for rejecting this possibility, the rate equations based upon this model also do not give any quantitative agreement with the experimental data.

APPENDIX C: ANALYTICAL SOLUTIONS OF EQS. (1) and (2) FOR THE PHOTOIONIZATION AT VERY LOW TEMPERATURES

At low temperatures ($e_{t1,2}=0$) or for very high photon fluxes Φ, the capture rates are very small in comparison to optical emission rates, so Eq. (2) becomes linear and can be solved analytically:

$$N_1(t) = \tfrac{1}{2}(N_D - N_A)e_2/(e_2 - e_1)$$
$$\times [\exp(-e_1 t) - \exp(-e_2 t)] , \qquad \text{(C1a)}$$

$$N_2(t) = \tfrac{1}{2}(N_D - N_A)\exp(-e_2 t) . \qquad \text{(C1b)}$$

In the experiments a change in the electron concentration is observed:

$$n(t) = (N_D - N_A)[1 - (\tfrac{1}{2}e_2 - e_1)/(e_2 - e_1)\exp(-e_2 t)$$
$$- \tfrac{1}{2}e_2/(e_2 - e_1)\exp(-e_1 t)] . \qquad \text{(C1c)}$$

Figure 8 shows the occupation of the defect D^- and D^0 charge states, as well as the electron concentration given by Eqs. (C1). It is seen that the occupation of the intermediate state D^0 for the photoionization process, depending on the ratio between e_1 and e_2, may reach high values for a certain period of time. An observation of the defect in this charge state is not possible for equilibrium ($t=0$) and metastable ($t \to \infty$) conditions. However, for some experimental techniques the equilibrium conditions are not necessary, and thus this charge state may be detected by, e.g., nonstationary ESR, or absorption.

A commonly used approach to study the photoionization process is to observe the initial slope of the photoconductivity transients. In our case this slope equals

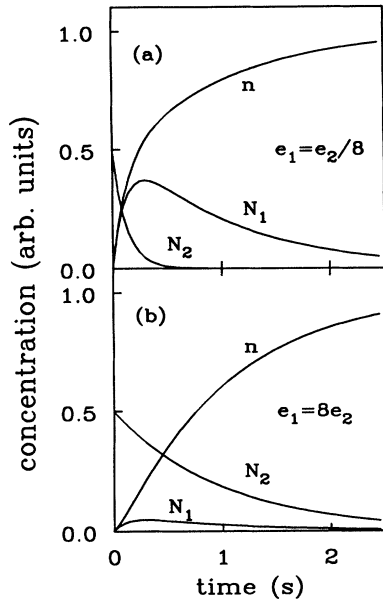$$dn/dt \ (t=0) = \tfrac{1}{2}e_{o2}(N_D - N_A) . \qquad \text{(C2)}$$

FIG. 8. Occupation of two charge states of a defect forming a negative-U system (N_1, N_2) and concentration of electrons in the CB (n) derived from the rate equations (1) and (2) and initial conditions (3a) for the case $c_1 = c_2 = 0$.

Equation (C2) shows that this method is sufficient only for investigation of the photoionization process of the D^- defect charge state. If in the experiment prior to the sample illumination any preillumination was applied, the initial conditions (3a) are not valid, and the initial slope methods give values of the photoionization rate being a complicated relation of e_{o1} and e_{o2}.

APPENDIX D: SPECTRAL DEPENDENCE OF THE PHOTOIONIZATION CROSS SECTION FOR A DEFECT STRONGLY COUPLED TO THE LATTICE VIBRATIONS

The first quantitative analysis of the photoionization spectrum for centers exhibiting LLR was performed for the bistable indium donor in CdF_2 crystals.[37] The model employed there assumes large displacements between the equilibrium configuration of the ground state and the ionized donor state. In the following, the same type of analysis is applied for the case of DX centers.

In systems with a large displacement between the equilibrium positions of the surrounding lattice for a defect in two charge states, the photoionization absorption cross section is given by

$$\sigma = \frac{A}{\sqrt{\pi}} \int_{-\beta}^{\infty} dz\, e^{-z^2} \sigma_{\rm el}(E_{\rm opt}, h\nu + E_b z)(1 + E_b z/h\nu) \,,$$

$$(\rm D1)$$

where A is a constant, $h\nu$ is the energy of incident radiation, $E_{\rm opt}$ is the electronic ionization energy, β is given by

$$\beta = (h\nu - E_{\rm opt})/E_b \,,$$

$$(\rm D2)$$

and the broadening parameter E_b is

$$E_b = \sqrt{2(E_{\rm opt} - E_{\rm th})\hbar\omega_0 \coth(\hbar\omega_0/2kT)} \,.$$

$$(\rm D3)$$

In the above formulas, $\hbar\omega_0$ is the vibronic energy of the lattice when the impurity is in the ground or the excited (ionized) state, and $E_{\rm th}$ is the energy of the defect in thermal equilibrium with the conduction band. The detailed shape of the electronic part of the photoionization spectrum $\sigma_{\rm el}$ is not critical for the shape in the tail region, which is governed by a Gaussian vibronic factor. For simplicity, a simple Lucovsky's formula for $\sigma_{\rm el}$ was used:

$$\sigma_{\rm el}(E_{\rm opt}, h\nu) = A \frac{(h\nu - E_{\rm opt})^{3/2}}{(h\nu)^3} \,.$$

$$(\rm D4)$$

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