Electron trapping by metastable effective-mass states of *DX* donors in indirect-band-gap $Al_xGa_{1-x}As$:Te

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Electron trapping by metastable effective-mass states of Te donors bound to the X minimum of the conduction band is reported. Their identification is based upon the analysis of a photoinduced metastable infrared absorption and thermally activated persistent photoconductivity in indirect-band-gap $Al_xGa_{1-x}As$. Analysis of Hall-effect measurements within a two-level donor model supports the hypothesis of a bistable character of *DX*-type donors.

I. INTRODUCTION

Some ten years ago Lang and Logan[1] and Nelson[2] discovered that group-IV and group-VI dopants in $Al_xGa_{1-x}As$ exhibit unexpected behavior for donors in covalent semiconductors. Among the most characteristic features, these donors exhibit a large Stokes shift in their ionization and metastability of free carriers optically excited from these defects. The latter constitutes the phenomenon of persistent photoconductivity (PPC). Donors responsible for such phenomena in III-V compounds are called *DX* centers. During the last decade the origin and behavior of *DX* centers became one of the most debated problems (see Refs. 3–10 for recent reviews). The reason is obvious: *DX* centers inevitably appear in *n*-type III-V–compound semiconductors and seriously affect the performance of many devices, e.g., that of high–electron-mobility transistors.[4,9(b),11]

Since the earliest investigations on *DX* centers there is little doubt that doping of $Al_xGa_{1-x}As$ by group-IV or group-VI elements is the direct cause of the creation of the *DX* centers. Their detailed atomic structure is controversial and no consensus has been reached so far.[3,5,12–21] The most critical test of any of the *DX*-center models is the explanation of the metastability effects. They are quite common in bulk semiconductors as well as in semiconductor layer structures[3,4,22–33] and are caused by barriers which cannot be passed by the carriers at low temperatures. In many cases these barriers are truly macroscopic[23–25] (e.g., at heterointerfaces or artificial doping inhomogeneities, like those occurring in *n-i-p-i* structures[24]) or they are produced by extended defects (charged dislocations, grain boundaries, etc.[25–27]). Evidence grows, however, that many of the observed metastability phenomena are inherent properties of deep point defects.[22,28–33] Barriers may result from differences in the lattice configuration around the defect for the two defect states,[22,23,31–33] or they may be also a consequence of strongly different electron localization.[22,34] Since the strength of the electron-phonon coupling depends critically on the localization of the electron wave function,[35] a strong change caused by any transition (e.g., photoionization, transition to excited states, etc.) manifests itself also in phenomena known as large-lattice-relaxation (LLR) effects.[22]

The most general framework of the theoretical description of this class of phenomena (sometimes called the extrinsic self-trapping) has been given in a series of publications by Toyozawa,[34] Emin,[36] and Rashba.[37] They predict a discontinuity in localization resulting from the competition between the long-range (Coulombic) and short-range (local-defect potential and acoustic-phonon coupling) forces. In the energy functional $E(\lambda)$, in which λ is the localization parameter ($\lambda \propto 1/a$, where a is the effective radius of the bound carrier), the long-range forces lead to an attractive term proportional to λ, while the short-range forces, being proportional to the local charge density, result in an attractive term proportional to λ. Such a functional produces either delocalized effective-mass states pinned to the relevant band minimum which should be corrected for polaron and central-cell effects or highly localized states which are much more strongly coupled to host lattice vibrations. If the thermal- ionization energies for both states are of the same order of magnitude, they should be separated by a barrier as indicated in Fig. 1. This barrier facilitates metastable population of the higher-lying state, which manifests itself by various persistent effects. As an important consequence of this most general approach to defect states in crystals, deep defects possessing a long-range Coulomb potential should also have delocalized effective-mass states. For defects exhibiting LLR behavior, these *hydrogenlike* states should, in most cases, be metastable states. Therefore such defects are *bistable* at low temperatures (Fig. 1).

It is just this feature which we want to prove as being characteristic for Te-related *DX* centers in $Al_xGa_{1-x}As$. This would provide a final proof of the validity of the LLR model of *DX* centers originally proposed by Lang and Logan.[1] Until now, such proof has been given only

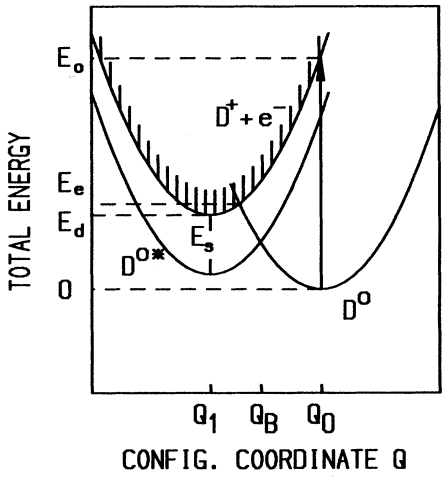

FIG. 1. Configuration-coordinate diagram of donors exhibiting large lattice relaxation.

for In and Ga donors in the highly ionic compound CdF_2.[38,39]

The essential difference between models predicting bistability of *DX* centers and other approaches consists in the way of accounting for the persistent photoconductivity effect. If the *DX* centers are bistable, then after ionization of their deep (*DX*) state, electrons would be transferred to the metastable excited effective-mass state of the same defect. This state is in thermal equilibrium with the conduction band at low temperatures and its depth determines the magnitude and temperature dependence of PPC: it should exhibit freeze-out with an activation energy related to the depth of the effective-mass-type shallow state.

This suggestion is difficult to prove for gallium-rich compositions of $Al_xGa_{1-x}As$ ($x<0.35$) with the Γ-point conduction-band minimum being the lowest one. For available intentional n-type doping levels ($N_D>10^{16}$ cm^{-3}) the thermal-ionization energy of the shallow donor, which is bound to the Γ-point conduction-band minimum, vanishes: an impurity band forms, which merges with the conduction band.[40] It is thus likely that a photoinduced infrared (ir) absorption in Si-doped $Al_xGa_{1-x}As$ (for $x<0.3$) reported by Theis *et al.*[41] is related rather to such an impurity band instead of the $1s$-$2p$ transition suggested. For the same reason, freeze-out of photoexcited carriers is not observed in transport measurements[2,42–44] suggesting excitation of electrons directly to the Γ-point conduction-band minimum. The situation is much more favorable for Al-rich $Al_xGa_{1-x}As$ compositions for which the X-point conduction-band minimum is the lowest one. In this case the shallow donor depth is larger [an estimate within the effective-mass approximation yields an ionization energy of $E_s\cong 40$ meV (Ref. 16)] providing a possibility of its observation.

The experimental evidence of the bistability of *DX* centers in $Al_xGa_{1-x}As$ presented in this paper, i.e., the conclusion that shallow and deep states are just two different appearances of the same physical object, is based on the observation of electron trapping on the metastable excited effective-mass state of the *DX* donor. The latter is derived from ir optical and Hall-effect experiments performed on indirect-band-gap Te-doped $Al_xGa_{1-x}As$ alloys. The ir absorption data have already been reported.[45] Here we present details of the experimental procedure as well as a more extended analysis. In the course of the present paper, we mostly followed the way which led us to the experimental proof of bistability of, analogous to the *DX* centers, In and Ga donors in the strongly ionic compound CdF_2.[7,38,39]

Quite recently the early suggestion[22(c)] of a similarity between the *DX* centers and negative-U defects in chalcogenide glasses has been debated.[6,7,20,46] There are several experimental results which are consistent with this suggestion. In the final part we discuss some of these results in more detail.

II. EXPERIMENTAL RESULTS

A. Photoionization of the *DX* ground state

1. *Samples and experimental details*

The samples used for photocapacitance experiments were $Al_xGa_{1-x}As$ layers grown by liquid-phase epitaxy (LPE). The structures were grown on n-type Te-doped GaAs substrates with a net electron concentration of $n>10^{19}$ cm^{-3}. These samples consist of a 3-μm n-type $Al_xGa_{1-x}As$ layer doped with $(1-2)\times 10^{17}$ cm^{-3} Te and a subsequent 4-μm p^+-type (doped with about 10^{19} cm^{-3} Ge) top layer of GaAs. The composition parameter x of the $Al_xGa_{1-x}As$ 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 p-n junction parameters were checked by current-voltage and capacitance profiling, and the energies for electron-emission and -capture processes were measured by the deep-level transient spectroscopy (DLTS) technique.

During the photocapacitance measurements samples were placed in a continuous-flow cryostat. A temperature controller enabled us to stabilize the sample temperature to better than 0.2 K. Optical-emission transients were detected using the SemiTrap DLS-82E spectrometer. A feedback circuit was employed to maintain a constant capacitance and the voltage applied to the diode was measured as a function of time. This technique allows one to avoid nonexponential transients due to large trap concentrations in the sample by keeping up a constant depletion width. As a source of a monochromatic light, a halogen lamp with a high-throughput prism monochromator was used. The photoionization cross sections were calculated from the emission time constant τ using the formula

$$\sigma^0(h\nu)=1/(\phi\tau)\ , \tag{1}$$

where ϕ is the photon flux, which had to be normalized at each wavelength according to the scaling curve obtained

for this illumination system. Time constants τ varied typically from 0.2 to 500 s. Longer transients could not be fitted with sufficient accuracy because even small temperature fluctuations cause distortion of the transients. At temperatures higher than 90 K, thermal emission was sufficiently fast to interfere with the slowest optical-emission transients.

2. *Photoionization spectrum shape analysis*

The photoionization spectra of the ground state of *DX*(Te) donors are presented in Fig. 2. Their shape and energetical position are similar to those reported earlier.[12] There is a very small shift in energy between the spectra corresponding to the two crystal compositions, indicating weak dependence of the electron ionization energy of the DX(Te) center on the alloy composition. A similar conclusion has been reached from a study of the *DX*(Si) center.[47] This indicates also that the Gaussian low-energy tail of the spectrum cannot be due to the broadening caused by alloy fluctuations.[48] Flattening of the spectrum with increasing temperature suggests phonon broadening. Such broadening is expected to occur if the LLR model of the *DX* center is valid. The first quantitative analysis of the photoionization spectrum for centers exhibiting LLR has been performed for the bistable In donor in CdF_2 crystals.[38] The model employed there assumes large displacements between the equilibrium configuration of the ground and ionized donor states. In the following, we will apply this analysis also in the case of *DX* centers.

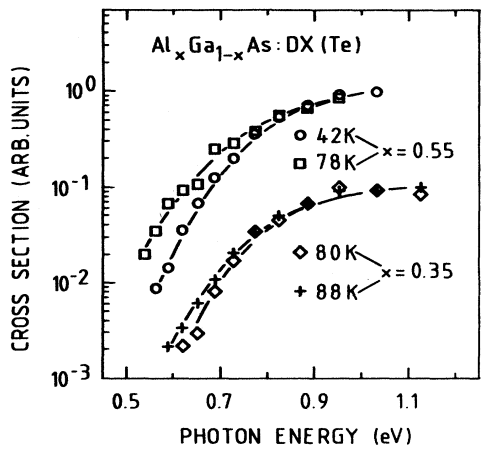

FIG. 2. Photoionization cross section for the deep *DX*(Te) state. The fitting parameters according to the large-lattice-relaxation theory (see text) are given in Table I.

In systems with a large displacement between the minima of the configuration curves (Fig. 1), a vibronic wave function of the excited state for the absorption process can be well approximated by a δ function centered on a classical turning point. Within this approximation, the photoionization-absorption cross section is given by[22,38]

$$\sigma(h\nu)=\frac{A}{h\nu}\sum_{n=0}^{\infty}p_n\int_{-\infty}^{\infty}dQ\int_0^{\infty}dE\,\rho(E)M^2(E)\chi_n^2(Q-Q_0)\delta(E_{\rm opt}+E-k_{\rm exc}(Q_0-Q_1)(Q-Q_0)-h\nu)\ , \tag{2}$$

where A is a constant, $h\nu$ the energy of incident radiation, p_n the thermal occupancy factor of the nth vibronic state of the ground electronic state, Q is the configurational coordinate, Q_0 and Q_1 denote the equilibrium lattice coordinate for the ground and ionized state, respectively, $\rho(E)$ is the density of the conduction-band states at energy E, $M^2(E)$ is the momentum optical electronic matrix element, $\chi_n^2(Q-Q_0)$ the vibronic overlap, and $k_{\rm exc}$ is the force constant of the excited electronic state. $E_{\rm opt}$ stands for the electronic (vertical) ionization energy corresponding to the lattice coordinate Q_0. Other symbols are explained in Fig. 1. Since the pure electronic cross section is given by the integral

$$\sigma_{\rm el}(E_{\rm opt},h\nu)=\frac{A}{h\nu}\int_0^{\infty}dE\,\rho(E)M^2(E)\delta(E_{\rm opt}+E-h\nu)\ , \tag{3}$$

and the sum $\sum_n p_n\chi_n^2(Q-Q_0)$ is given by Mehler's formula,[49] the broadened cross section of the photoionization process equals

$$\sigma=\frac{1}{\sqrt{\pi}}\int_{-\beta}^{\infty}dz\,e^{-z}\sigma_{\rm el}(E_{\rm opt},h\nu+\Gamma z)\left[1+\frac{\Gamma z}{h\nu}\right]\ , \tag{4}$$

where

$$\beta=\frac{(h\nu-E_{\rm opt})}{\Gamma}\ , \tag{5a}$$

and the broadening parameter Γ is

$$\Gamma=\hbar\omega_{\rm exc}\left[\frac{2(E_{\rm opt}-E_{\rm th})}{\hbar\omega_0}\coth\left[\frac{\hbar\omega}{2k_BT}\right]\right]^{1/2}\ . \tag{5b}$$

In the above formulas, k_0 is the force constant of the ground electronic state and $\hbar\omega_0$ and $\hbar\omega_{\rm exc}$ are the vibronic energies of the lattice when the impurity is in the ground or the excited (ionized) state, respectively.

The detailed shape of the electronic part of the photoionization spectrum $\sigma_{\rm el}(h\nu)$ is not critical for the shape in the tail region which is governed by a Gaussian vibronic factor. For simplicity we have substituted a simple Lucovsky formula[50] for $\sigma_{\rm el}(h\nu)$:

$$\sigma_{\rm el}(h\nu)=A\frac{(h\nu-E_{\rm opt})^{3/2}}{h\nu}\ , \tag{6}$$

as it has already been done successfully in the case of In in CdF_2.[38] Other authors[12,47] have used a multiparameter formula for $\sigma_{\rm el}$, but as the Gaussian tail governs the quality of the fit, such a procedure seems neither to be necessary nor valid at present. Table I summarizes the

TABLE I. Optical ionization energy E_{opt} and the broadening parameter Γ of the deep DX-state photoionization spectrum of DX(Te) centers in $Al_xGa_{1-x}As$:Te presented in Fig. 2. $n_{300\,K}$ is the room-temperature electron concentration derived from C-V measurements.

x	$n_{300\,K}$ (cm^{-3})	T (K)	E_{opt} (eV)	Γ (eV)
0.35	1.1×10^{17}	80	0.70	0.10
		88	0.70	0.12
0.55	2.0×10^{17}	42	0.69	0.11
		78	0.66	0.14

data obtained from the fitting procedure. The high quality of the fit, as well as the temperature trends in the broadening parameters, strongly support the hypothesis of the localized nature of the ground state of the DX center and the large lattice displacement occurring during the ionization process. It should be also emphasized that a similar conclusion on a very localized character of the ground-DX(Te)-state center in $Al_xGa_{1-x}As$ has been reached from the analysis of the influence of alloy fluctuations on the thermal capture and emission as seen in DLTS experiments.[51]

B. Photoionization of shallow excited states of DX centers

1. Samples and experimental technique

Tellurium-doped samples of $Al_xGa_{1-x}As$ grown by liquid-phase epitaxy (LPE) on (100)-oriented semi-insulating GaAs:Cr substrates have been used for optical-absorption measurements. Since the intended Te concentration was in the range of 10^{16} cm^{-3}, thick (20–50 μm) layers had to be grown in order to reach sufficient optical density. The gradient in Al content along the growth axis was measured by an electron microprobe. Results, including error bars, are depicted in Fig. 3.

Infrared absorption was measured after cooling the samples in darkness down to 10 K, using a rapid-scan Fourier spectrometer. The metastable, light-induced absorption, as given in Fig. 4 for various samples of different compositions, has been recorded after illumination by a tungsten-halogen lamp. The "dark" absorption has been subtracted. After switching off the halogen lamp the spectra remain stable during a one-day-measurement run, thus proving metastability of the photoinduced absorption. The absorption which is metastable at $T=10$ K disappears once the sample temperature is raised above about 100 K, and after that the whole experiment can be repeated with the same result.

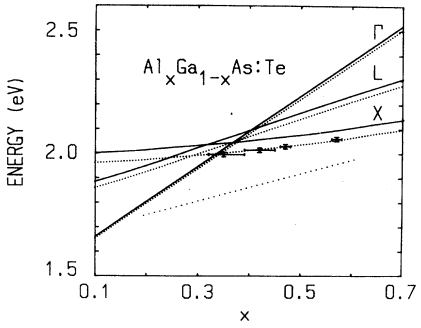

FIG. 3. Conduction-band minima and DX donor levels in $Al_xGa_{1-x}As$. The points represent the optical ionization energy of the metastable photoinduced shallow state of the Te DX center.

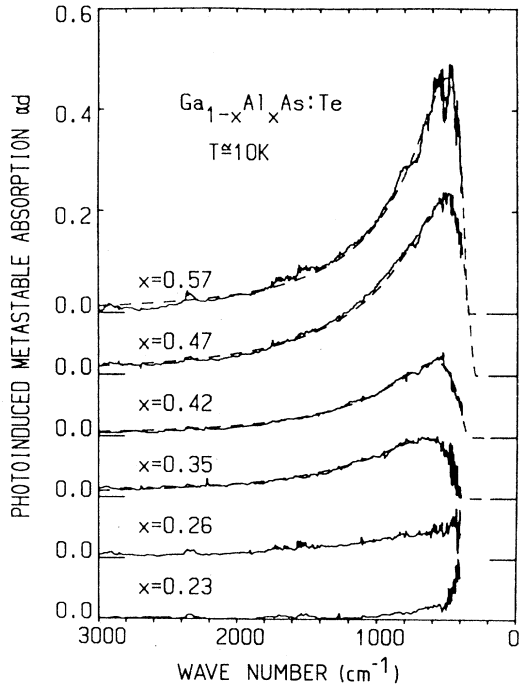

FIG. 4. Photoinduced metastable absorption in $Al_xGa_{1-x}As$:Te. Dashed lines denote the fitted photoionization spectra (see text).

2. Shape analysis of the metastable ir absorption

The most remarkable feature of the photoinduced absorption is the fact that its peak position and the extrapolated low-energy cutoff are almost independent of composition for $x>0.35$. The overall shape of the absorption spectra suggests photoionization as their origin. As the energy range of this absorption corresponds well with estimates of the ionization energy of the shallow donors bound to the X-point conduction-band minimum,[16] it is tempting to compare it with the well-known ir absorption in GaP due to shallow impurity donors.[52] The major difference is the lack of a fine structure due to transitions to higher excited effective-mass states of a donor. At present, the reason for the lack of such structure is not clear. It may be due to the local composition fluctuations (broadening due to alloying). Another reason for broadening is the influence of the local fields originating from doping.[53] Quite similar problems occurred in an early stage of studying shallow donors in CdF_2.[54] With insufficient crystal purity, only a structureless photoion-

ization spectrum of the shallow ($E_D \approx 100$ MeV) donor states has been seen.[38,54] Later on, when we succeeded in growing much less compensated and purer crystals, a sharp line spectrum below a photoionization continuum due to the transitions to the excited states occurred.[39] It should be noted, however, that the value of the ionization energy of shallow donor states in CdF_2 (as estimated from a fitted threshold of the structureless photoionization spectrum) has later been confirmed by the analysis of the ir photoconductivity and the ir absorption due to transitions to excited states of the donors.[39] Relying on this experience we have fitted the shape of the photoinduced metastable absorption with the following formula for the photoionization cross section $\sigma(h\nu)$:

$$\sigma(h\nu)=C(h\nu-E_s)^A/h\nu^B , \tag{7}$$

where E_s is the shallow donor ionization energy and A,B,C are fitting parameters. This formula is a most simple generalization of different models which describe the impurity photoionization cross section within the effective-mass approximation.[50,55–57]

The shape of the impurity photoionization spectrum is governed mainly by three factors. (i) The density of final states in the conduction band, $\rho(E_k)$. (ii) The square of the momentum matrix element $p_{ic}(k)$ between the Bloch functions of the nearby band and the appropriate Bloch function entering the impurity wave function. (iii) The square of the Fourier transform $\phi(k)$ of the impurity envelope $F(r)$ function:[58]

$$\sigma(h\nu)=\frac{D}{h}\rho(E_k)p_{ic}^2(k)\phi^2(k) , \tag{8}$$

where D is a constant.

The first two factors [(i) and (ii)] define a threshold dependence on the electron energy in the final state within the conduction band $E_k=h\nu-E_s$. The Fourier transform $\phi(k)$ of the donor envelope function depends rather on the total photon energy, $h\nu$, than on F_k.

Let us consider two extreme localization cases. The first is a hydrogenlike $1s$ state, for which the envelope $F(r)$ is proportional to $\exp(-r/a)$, a being the Bohr radius. For such a state, the square of its Fourier transform $\phi^2(k)$ is proportional to $1/(h\nu)^4$ according to

$$\phi(k)\propto[(1/a)^2+k^2]^{-2}\propto(E_s+E_k)^{-2} . \tag{9}$$

Another extreme is a δ-like binding potential (the Lucovsky model[50]), for which the envelope $F(r)$ is proportional to $r^{-1}\exp(-r/a)$. This dependence produces much weaker energy dependence: $\phi^2(k)$ is approximately proportional to $1/(h\nu)^2$. This proportionality results from the relation

$$\phi(k)\propto[(1/a)^2+k^2]^{-1} . \tag{10}$$

For such centers, the relationship between a and E_s is less straightforward, and hence Lucovsky's result $\phi^2(k)\propto 1/(h\nu^2)$ must be taken with care. An intermediate case is reproduced by a quantum-defect model[55] or a billiard-ball model.[56] In both cases, the energy dependence of $\phi^2(k)$ is intermediate between the Lucovsky model[50] and the hydrogenic model.

For a parabolic and spherical band the density of states is

$$\rho(E_k)\propto(h\nu-E_s)^{1/2} . \tag{11}$$

If the donor wave function is built predominantly from a nearby, parabolic conduction-band minimum, the momentum matrix element should be linear in k ("forbidden" transitions). This produces a proportionality

$$p_{ic}^2(k)\propto k^2\propto h\nu-E_s . \tag{12}$$

Therefore, for a spherical and parabolic case, a general form of the donor photoionization spectrum is given by Eq. (7) with $A=\frac{3}{2}$ and $3\le B\le 5$, depending on the type of binding potential. It should be stressed, however, that the model calculations outlined above are performed within the Born approximation (the Coulomb effects for the electron states in the conduction band are neglected).[57] Therefore, one cannot rely too much upon the quality of the fit to experimental data in the region close to the threshold where an additional influence of broadened discrete transitions to excited donor states is possible. Conclusions reached from a study of the region well above the threshold, in which $\sigma(h\nu)$ is proportional to $(h\nu)^{A-B}$, are much more reliable.

As in GaP, in indirect-band-gap $Al_xGa_{1-x}As$ the lowest conduction-band minimum is of X symmetry. The parabolic and spherical approximations used above are therefore invalid. Following arguments by Kopylov and Pikhtin,[52] the momentum matrix element becomes practically constant some 0.2–0.3 eV above the photoionization threshold. This would produce a value of A close to $\frac{1}{2}$. The conduction band, however, is strongly nonparabolic and therefore, the density of states grows faster than in the parabolic case, partially compensating the decrease of A due to the decreasing momentum matrix element. Another complication arises from the strong anisotropy of the effective mass. Taking that into account produces much weaker dependence of $\phi^2(k)$ than in the spherical symmetry case. For a simple Coulomb potential, $\phi^2(k)$ is proportional to $(h\nu)^{-3}$ only.[52] Taking all these factors into account, one can expect much weaker dependence of the high-energy photoionization tail for indirect-band-gap semiconductors in comparison with the simple parabolic and spherical symmetry case.

Fitting parameters for the spectra shown in Fig. 3 are summarized in Table II. The values of $A\cong 1.5$ and $B\cong 4$ obtained from a fit of Eq. (7) to the experimental data are in reasonable agreement with the considerations presented above. The most important result of these fits is the energy dependence of the photoionization high-energy tail. It is proportional to $h\nu^{B-A}$, with the value of $B-A$ close to 2.5 for all samples. A similar value was obtained[52] for the photoionization of shallow donors in GaP, thus providing strong support for our model of the shallow DX-impurity state being pinned to the point-X conduction-band minimum. This conclusion finds strong support also in recent measurements of electron-spin resonance on the metastable photopopulated shallow donor states in indirect-band-gap $Al_xGa_{1-x}As$ doped with Si.[59,60] Analysis of the g factor clearly indicates the X-

TABLE II. Sample parameters of $Ga_xAl_{1-x}As$:Te layers of thickness d, in which the photoionization spectrum shown in Fig. 4 was seen. The estimated rms deviation of the fitting parameters E_s, A, and B are 5 meV, 0.4, and 0.2, respectively. The room-temperature Hall carrier concentration $n_{300\ K}$ for these samples can be regarded as an estimate of the order of magnitude of the doping concentration only (see discussion in the next chapter).

x (%)	d (μm)	$n_{300\ K}$ (cm^{-3})	E_s (meV)	A	B
23±5	52	2.3×10^{18}			
26±4	45	3.8×10^{16}			
35±3	40	1.0×10^{16}	49	1.5	2.3
42±2	45	1.4×10^{16}	43	1.8	2.6
47±1	19		39	1.6	2.5
57±1	28	2.6×10^{16}	42	1.3	2.7

like character of the metastable state. It is also supported by a constancy of the threshold energy as well as its value ($E_s \cong 45$ meV).

The shallow metastable states should participate also in low-temperature donor-acceptor recombination. The localized, deep DX states, in contrast, cannot participate in it due to the immeasurably long capture lifetime. Dingle *et al.* have observed[61] in the D-A recombination donors of similar depth as found by us. Recent optically detected magnetic resonance (ODMR) investigations of this luminescence, but related to Si donors,[62] clearly indicate the X-like nature of the shallow donor state participating in the emission. Finally, the metastable character of the shallow donor state manifests itself also in the persistent character of the low-temperature luminescence.[63]

C. Hall-effect measurements

The optical measurements clearly indicate that shallow effective-mass donor states are populated after photoexcitation of DX levels. They do not allow one, however, to prove quantitatively that the number of metastable states is equal to the number of centers producing DX states. This equality is required within the present model of bistability of the DX centers. In principle, the number of shallow states could be derived from the absolute optical-absorption amplitude, taking into account the exact shape of the envelope function, which is not available, however. Therefore, in order to check whether all DX centers are transformed to shallow donors, we have measured the temperature dependence of the electron concentration for indirect-band-gap $Al_xGa_{1-x}As$:Te, before and after photoexcitation by means of Hall-effect investigations.

If the shallow states belong to the same center as the DX-like states (i.e., the deeper states characterized by a large Stokes shift in their ionization and immeasurably long capture lifetimes at low temperatures), then at low temperatures they should govern all transport properties of the host material after photoexcitation. In contrast to the ground state, their coupling to the lattice should be small and then they should be in a "thermodynamic" equilibrium with the conduction-band states: photoexcited carriers must be distributed between the conduction band and these states according to the standard Fermi-Dirac statistics without taking into account the deeper DX states (either empty or filled). Therefore, beyond the direct-indirect crossover the persistent, photoinduced conductivity (PPC) must exhibit low-temperature freeze-out: its magnitude in this temperature range must become smaller. Before crossover, capture of carriers at low temperature occurs only by shallow Γ-like states. Since they form an impurity band even at relatively low doping concentration the freeze-out upon them can be simply disregarded. After crossover, the much deeper X-like states must participate in a carrier repopulation and thus, the magnitude of the PPC must decrease. This is exactly the behavior reported by Chand *et al.* for Si donors.[44]

Additional motivation for more detailed transport measurements derives from controversies in the sign of mobility changes under PPC conditions.[2,43,44,64]

1. *Samples and experimental details*

A set of moderately Te-doped ($N_D < 10^{18}$ cm^{-3}), (1–4-μm-thick LPE layers of $Al_xGa_{1-x}As$ with different compositions ($0.3 < x < 0.7$) were grown directly on semi-insulating (SI) Cr-doped GaAs. Since modulation-doping effects have been found in these samples, we have investigated specially prepared structures with a low-Ge-doped ($p \cong 10^{16}$ cm^{-3}) buffer layer, separating n- type $Al_xGa_{1-x}As$:Te from the SI GaAs:Cr substrate. Since modulation doping has not been reported for the indirect-band-gap $Al_xGa_{1-x}As$ and the results obtained by us may help in clarifying some controversies concerning the mobility changes, we report here results for both types of samples.

Samples of van der Pauw geometry were prepared with evaporated Al-Au/Ge Ohmic contacts alloyed at 450 K for 5 min to the surface of the $Al_xGa_{1-x}As$ layer. Measurements were done with the sample mounted to the cold finger of a closed-cycle refrigerator. The sample was shielded from ambient light and background radiation by a closed cold shield. Illumination at low temperature was facilitated by an ir-light-emitting diode ($\lambda > 850$ nm) mounted within the cold shield. The Hall concentration was measured during cooling the sample in darkness and then the sample was illuminated at low temperature ($T < 50$ K) and measured again in darkness during heating up.

2. Results

(a) Samples without a buffer layer. For a direct-band-gap sample ($x=0.3$) at low temperatures (within the metastability regime at $T<100$ K) a pronounced increase of the Hall concentration is observed after illumination of samples cooled in darkness (Fig. 5), similar to that reported previously for LPE-grown direct-band-gap $Al_xGa_{1-x}As$:Te.[2] For indirect-band-gap samples ($x>0.4$), in contrast, the amplitude of PPC was smaller by orders of magnitude and the apparent electron concentration (either in darkness or after illumination) was temperature independent. Simultaneously, the apparent mobility at 100 K reached $(4-5)\times10^3$ cm^2/V s for all samples and decreased after sample illumination. Therefore, we conclude that a high-mobility channel is formed at the $Al_xGa_{1-x}As$/GaAs interface and modulation doping of the channel takes place, similar to what is observed in direct-band-gap molecular-beam-epitaxy (MBE)–grown samples.[42,43] In this case, complicated multilayer conduction occurs and PPC is not a specific property of the $Al_xGa_{1-x}As$ layer anymore. Especially under illumination, the apparent mobility strongly decreases. This effect is analogous to that reported for Te donors in LPE-grown samples by Nelson[2] and Si-doped MBE samples by Collins,[43] and we attribute it to the modulation-doping effect, as evidenced by the opposite behavior of samples with a buffer layer (see next section).

(b) Samples with a buffer layer. Results are qualitatively different (Fig. 6) for a LPE-grown sample of Te-doped $Al_xGa_{1-x}As$ ($x=0.57\pm0.2$, $d=3$ μm) on top of a Ge-doped ($p\cong10^{16}$ cm^{-3} $d=0.5$ μm) buffer layer of the same composition. As before, a (100)-oriented GaAs:Cr substrate is used. This buffer layer prevents formation of an interface n-type channel and modulation-doping effects. During all measurements, voltages smaller than 1 V were used in order to prevent participation of the p-type layer in the current through the sample.

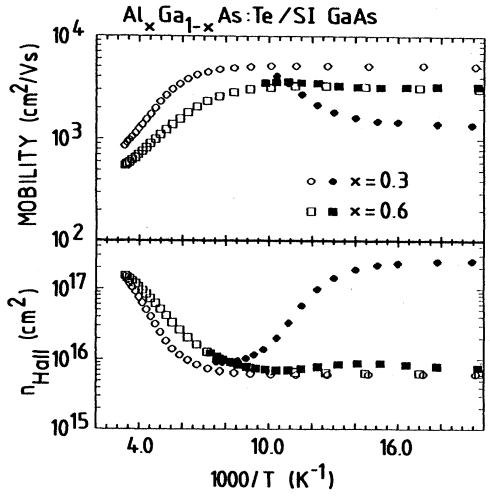

FIG. 5. Hall mobility and concentration for direct-band-gap ($x=0.3$) and indirect-band-gap ($x=0.6$) n-type $Al_xGa_{1-x}As$:Te grown by LPE directly on SI GaAs:Cr. Open symbols denote values measured during cooling the sample in darkness, solid ones during heating up in darkness after illumination below 50 K.

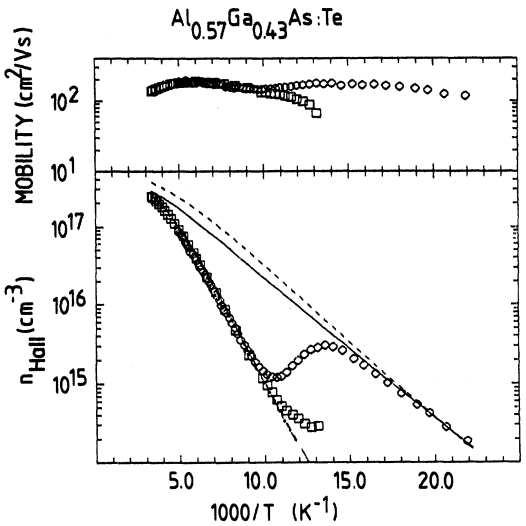

FIG. 6. Hall mobility and concentration for an indirect-band-gap n-type $Al_xGa_{1-x}As$:Te ($x=0.57\pm0.02$) LPE layer separated by a thin p-type $Al_{0.57}Ga_{0.43}As$ buffer layer from the SI GaAs:Cr substrate. Squares denote data taken during cooling in darkness, circles are obtained during the heating in darkness after illumination below 50 K. The lines represent theory within the two-level donor model (see text). Solid and dashed lines represent the expected persistent-photoconductivity behavior with all electrons transferred to the shallow donor states in the weak- and the strong-compensation case, respectively.

The measured mobility of $\mu\approx150-200$ cm^2/V s in the whole temperature range indicates that indeed only electrons in the X-point conduction-band minimum contribute to the transport. A pronounced increase in electron concentration after illumination at low temperatures is observed in darkness below 100 K. Simultaneously, the electron concentration is no more constant under metastability conditions (below 100 K). It decreases with decreasing temperature and exhibits well-defined activation character. The activation energy is slightly smaller than half of the activation energy in the high-temperature range in which the deep ground DX level governs the electrical transport. Simultaneously, a slight *increase* in mobility under PPC conditions has been observed.

3. Analysis of Hall-effect measurements

In the temperature dependence of the carrier concentration (Fig. 6) there are two temperature regions in which equilibrium statistics applies. In the high-temperature region (well above 100 K), the capture barrier is ineffective and under standard measurement conditions all DX-related states participate in the carrier distribution between conduction band and defect states. At low temperatures (below 60 K), however, the deeper DX state is switched off from the carrier exchange. After photoexcitation, only the shallow state participates in the carrier exchange between the conduction band and the

DX-center-related states. Let us denote by N_s the concentration of ionized DX donors which at low temperatures can accept electrons photoexcited from the deeper DX state at shallow states. The thermal depth of these shallow states is designated by E_s and their degeneracy factor by g_s. If photoexcitation causes ionization of the deep DX states producing N_0 electrons, then the equilibrium carrier concentration n is a solution of the equation

$$\frac{n(N_s-N_0+n)}{N_0-n}=\frac{N_C}{g_s}e^{-E_s/k_BT}, \tag{13}$$

where N_C is the conduction-band density of states. Since in our case the equilibrium carrier concentration n is smaller than 5×10^{15} cm^{-3} the following solution similar to the well-known strong-compensation limit[65] is valid:

$$n=\frac{N_C}{A}e^{-E_s/k_BT}, \tag{14}$$

where $A=g_s(N_s/N_0-1)$. Suppose at first that the occupied DX center is a neutral deep donor possessing two kinds of states: the deeper DX-like state and the shallower effective-mass state. Then the number of the ionized DX centers which can accept electrons at the shallow state is $N_s=N_0+N_A$. At the same time the number of occupied deeper DX states is $N_d=N_D-N_0-N_A$, N_D being a total concentration of the DX centers. A fit to the experimental data in the low-temperature PPC range of Eq. (14) with the density of states characteristic of the point-X-minimum conduction-band minimum ($m^*=0.81$) (Ref. 40) yields an activation energy E_s close to 25 meV and a value of $A=10$.

Statistics becomes more complicated if the DX centers exhibit a negative-U behavior.[9(a),66] In that case, the deep DX state would be a negatively charged two-electron state. After sample cooling in darkness, the number of these two-electron states (DX states) is $N_d=(N_D-N_A)/2$ and the number of shallow empty states (ionized DX donors) is $N_s=(N_D+N_A)/2$, which can be much larger than in the previous case if $N_D\gg N_A$. Now, liberation of N_0 electrons from the occupied deep DX states increases N_s by $N_0/2$ since the deep state is occupied by two electrons. Equations (13) and (14) are still valid, but we should substitute now $(N_D+N_A+N_0)/2$ for N_s and just (N_0+N_A) as in the previous case.

If all deep DX states are photoionized, then N_s equals N_D in both cases and the same carrier statistics applies. In either case, the electron activation energy in the low-temperature region is expected to be just a thermal depth E_s of the shallow state according to Eq. (14). That energy is in our case 25 meV, in good correspondence with the optical data. Higher doping should result in a decrease of this value which is most probably the reason for smaller values of E_s obtained recently by Mizuta and Mori in $Al_xGa_{1-x}As$ heavily doped with Se.[67]

Interpretation of the high-temperature region is less straightforward. The activation energy of the carrier concentration is now governed mainly by the deep DX state. The shallower state should be included in the statistics as the excited state of the donor (in the normal case of $U>0$) or just as another charge state (if the DX center exhibits a negative-U behavior).[66] Neither of these alternatives can be ruled out from a simple analysis of the temperature dependence of the carrier concentration.[20,66] We have therefore applied a standard fitting procedure[65] assuming that the occupied DX centers are deep donors. In this analysis (no modulation-doping condition) we have assumed that only electrons from X-point conduction-band minima contribute to the transport (we are far enough from the crossover of Γ- and X-point conduction-band minima). A value 0.81 of the density-of-states effective mass has been used. We have also allowed for a temperature dependence of the ionization energy E_d of the deep DX state. In fact, E_d is the change of Gibbs free energy and can be described as $E_d=H_d-TS_d$, where H_d is the enthalpy and S_d the entropy of ionization. Now the carrier concentration n is governed by the equation[65]

$$\frac{n(n+N_A)}{N_D-N_A-n}=\frac{N_C}{g_d\exp(E_d/k_BT)+g_s\exp(E_s/k_BT)}. \tag{15}$$

In the fitting procedure, a value of the deep state degeneracy factor $g_d=2$ has been assumed. We have also assumed total photoionization of the deep DX states to be able to include also the data in the low-temperature range in an iteration procedure. Since in the PPC regime back-population of the deep DX state is not possible, the term $\exp(E_d/k_BT)$ has been omitted in this temperature range. An iteration procedure has been used to evaluate all parameters: the donor concentration N_D, the acceptor dentisty N_A, and the energies E_d and E_s. As usual, two sets of parameters corresponding to strong and weak compensation have been obtained. For weak compensation (inconsistent with the former analysis of the PPC region alone as well as with the fact that the Fermi level in the whole high-temperature range lies below the deeper state) $H_d=148$ meV, $S_d=0.33$ meV/K, $E_s=62$ meV, $N_D=3.8\times10^{17}$ cm^{-3}, and $N_A<10^{14}$ cm^{-3}. For strong compensation (see fit in Fig. 5) $H_d=70.5$ meV, $S_d=0.10$ meV/K, $E_s=30.3$ meV, $N_A=7.6\times10^{17}$ cm^{-3}, and $N_D-N_A=4.9\times10^{17}$ cm^{-3}.

We have also tested the influence of the value of the degeneracy ratio g_s/g_d on the quality of the fit. A higher value of this parameter implies that we neglect a valley-orbit splitting for the X-bound effective-mass state. It leads to a slight decrease of the quality of the fit, but as we do not know anything about a degeneracy of the ground DX state, this result does not provide much information. Also setting the entropy factor equal to zero does not affect the fit significantly in the strong-compensation limit. Therefore, a discussion of the influence of that carrier concentration on this factor (important for a distinction between negative-and positive-U cases[9,68,69]) is not conclusive in this case.

A similar analysis can be carried out assuming a negative-U character of the DX donor. Then the ground D^- state should be acceptorlike, but in contrast to the above considerations, its ionization energy E_D should be

replaced by $2E_D$ as its ionization frees two electrons bound at this state. A major difference in statistics results from the fact that in the ground state of the system half of the *DX* states are empty, equivalent to strong compensation at $U>0$. Neglecting the contribution of the excited state, Eq. (15) becomes now

$$\frac{n^2(n+N_A+N_D)}{N_D-N_A-n}=N_c^2\exp\left[-\frac{2E_D}{k_BT}\right], \tag{16}$$

the degeneracy factor being incorporated in the entropy part of E_D. Obviously for most reasonable doping conditions the solution of this equation is equivalent to a strong-compensation limit in the positive-U case considered above. Therefore, unless one knows real donor and acceptor concentrations from other experiments, the temperature dependence of the equilibrium concentration hardly provides a distinction between positive- and negative-U cases.

In many papers concerning *DX* centers, the existence of independent shallow and deep donors has been assumed.[42,70,71,72] It is also possible to follow such a formal procedure here and we obtain again a reasonable fit to the experimental data. A simple analysis of all published results in the indirect-gap-band-region (to assure that the shallow states will not form an impurity band) leads to the conclusion that independent of donor dopant, the way it has been introduced and its intended concentration, a strong compensation is necessary in all these cases, which is not plausible at the present state of the art in the growth of epitaxial layers of $Al_xGa_{1-x}As$. This conclusion arises from the following considerations.

In the indirect-band-gap region, freeze-out in the PPC regime has always been seen,[44,67,73] similar as in our case (this freeze-out is responsible for the dramatic decrease of the PPC amplitude in the indirect-band-gap region observed by Chand *et al.*[44]). This implies that the concentration of the shallow centers N_s must be larger than the number of uncompensated deep states N_d. Otherwise after ionization of deep states at low temperature (in the PPC regime) a leveling off of the free-carrier concentration should occur, i.e., some electrons excited to the conduction band should not be able to find empty shallow states to be retrapped. Lack of leveling off under PPC conditions means that in all cases $N_d<N_A$ (in our case $N_d-N_a<10^{14}$ cm^{-3}). A similar condition must be fulfilled by the shallow states, i.e., $N_s<N_A$, since in all cases in the high-temperature region there is no trace of the locking of the Fermi level to a shallow state and the temperature dependence of the electron concentration is governed by the deep *DX* state. Summing up both conditions results in a very strict and unusual compensation condition:

$$N_A<N_a+N_d<2N_A\ . \tag{17}$$

If the concentrations of the shallow and the deep (*DX* centers) donors differ strongly, the above condition is equivalent to almost total compensation. Such a conclusion is reached when analyzing all published results within the above model. This analysis indicates that in most cases the above condition is even more stringent, namely $N_s+N_d<\beta N_A$ with β much smaller than 2 (in our case it is close to 1.1). It indicates a strong compensation in all cases, a highly unlikely event, especially in the heavily *n*-type doped samples used by Mizuta and Mori.[68] It should be also pointed out that recent studies of *DX* centers in heavily *n*-type doped GaAs[8,74,75] indicate that *DX* centers occur always in concentrations very close to the chemical donor doping density, the result being in direct conflict with the early idea of independent shallow and deep donors.

III. DISCUSSION AND CONCLUSIONS

From the early beginning of investigations of *n*-type $Al_xGa_{1-x}As$ many models of *DX* centers were formulated. Several authors[42,70,72] suggested, that group-IV or -VI impurities introduced into the crystal may form either *deep* (*DX*) or *shallow* states, and the *sum* of both may reach the number of introduced dopants. Thus fixed (and mutually independent) numbers of deep and shallow centers were considered when analyzing transport properties of $Al_xGa_{1-x}As$ or in modeling multilayer parallel conduction of high-electron-mobility transistor (HEMT) structures.[76] There is growing evidence, however, that the number of *DX* centers equals the number of chemical donor dopants[4,8,9,10,74] and, as discussed above, the shallow states are just excited states of the *DX* centers and not due to an independent species.

The most debated issue is the physical nature and origin of the deep state of *DX* centers. In general, two classes of models are discussed. They differ in the strength of the defect-lattice coupling. One class of models follows the original proposal by Lang and Logan,[1] who postulated a very strong defect-lattice coupling. This assumption leads to a large lattice relaxation (LLR).[4–9,12,16,20,45] Another class of models assumes a weak coupling and thus leads to a small lattice relaxation (SLR).[17–19] Some models, especially those involving LLR, predict *bistability* of the *DX* donor (Fig. 1). The donor possesses two states of different localization: the ground localized deep (*DX*) state exhibiting large lattice relaxation and an excited effective-mass state derived from the nearby conduction-band minimum without lattice relaxation. Both states are separated by a vibronic barrier leading to the metastability shown by *DX* centers at low temperatures.

The experimental results presented in this paper provide strong support of the LLR model. The observation of a photoinduced metastable absorption clearly shows that the shallow effective-mass state originating from the nearest conduction-band minimum is populated after ionization of the deep *DX* states. Analysis of Hall data shows that the *DX* center can be well described within the framework of a two-level donor model with the higher state metastably photopopulated at low temperatures after photoionization of the ground state.

Our results provide, therefore, strong support for the hypothesis that the shallow state is just an excited state of the deep *DX* state and, consequently, for the bistability of these impurities. The ground *DX* state of the *DX* center is highly localized. The temperature dependence of its

photoionization spectrum is consistent with a vibronic origin of a broadening of this transition in accordance with the LLR model. This model also provides a natural explanation of the metastability occurring after photoionization of the deep *DX* state.

In several SLR models metastability has been argued to result from selection rules forbidding transitions between the defect states connected with different conduction-band minima (e.g., the ground *DX* state being derived from the *L*-point conduction-band minimum and the other states from Γ- and *X*-point conduction-band minima). Such selection rules, however, cannot lead to practically infinite lifetimes of the excited states of the *DX* centers at low temperatures. For localized defects the electron wave function must be constructed from more than a single nearby minimum and thus, the above-mentioned selection rules lose their strictness and validity. This is exactly the case for the ground localized state of a *DX* center, for a long time advocated as originating from the *L*-point minimum of the conduction band.[16–18] Such pinning is, as pointed out by Chadi and Chand,[20] only apparent. Also recent results on the pressure influence on the localized *DX* state do not support such pinning. They indicate rather that the pressure coefficient of the level energy differs from the analogous coefficient of the *L*-point conduction-band minimum.[77]

Finally it may be concluded that all characteristic features of the *DX* centers validate the LLR models of these donors. The system possesses all attributes of the Toyozawa model of extrinsic self-trapping:[34] two states of different localization are separated by a vibronic barrier which facilitates metastable population of the higher one.

Recently the idea that *DX* centers may constitute a negative-*U* system[22(c)] reappeared.[6,7,20,46,78] This idea, however, cannot be positively verified by now. There are some indications in favor of this model as, e.g., lack of an ESR signal suggesting diamagnetic character of the ground *DX* state and an increase in mobility after photoionization of the deep *DX* state observed in lightly doped (nondegenerate) layers of $Al_xGa_{1-x}As$ (see, e.g., Fig. 5 and Refs. 9, 44, 46, and 64), they cannot be regarded as final proofs.

The mobility enhancement has been observed in lightly doped samples, which are usually highly compensated. In such samples, the formation of band tails occurs. Filling of these tail states by photoexcited carriers may lead to a slight enhancement of their mobility [for a more extensive discussion of such a case, see Ref. 22(a) in a context of CdTe:Cl].

Lack of an ESR signal of the *DX* ground state can result either from its diamagnetic character (consistent with a negative-*U* hypothesis) or just from a very large broadening of the ESR signal for the highly localized centers.[59,60] The latter explanation is supported by recent investigations of the magnetic susceptibility of $Al_xGa_{1-x}As$:Si which are interpreted in terms of a paramagnetic, single-electron ground state and hence, of a positive-*U* system.[79]

The recent observation of an anomalously slow transient of the near-band-edge photoluminescence[63] has been tentatively discussed in terms of light-induced conversion of the deep *DX* centers into shallow donors and the experimental finding of a very small initial intensity was argued to be inconsistent with a negative-*U* model.[63] More detailed investigations, however, revealed hole capture as the mechanism responsible for the anomalous time dependence of photoluminescence.[80] Therefore, at present, this effect does not allow to decide about the negative-*U* model either.

In conclusion, *DX* centers are bistable donors with a shallow-deep bistability resulting from a large lattice relaxation. It is also highly unlikely that the formation of a stable defect complex is a prerequisite for the *DX*-center formation. Further progress in the understanding of *DX* centers depends crucially on the experimental identification of its ground state with respect to charge, spin, and the microscopic structure.

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