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DX center in $Ga_{1-x}Al_xAs$ alloys

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From the electron-emission and -capture variations with the alloy composition, we deduce that the *DX* center in $Ga_{1-x}Al_xAs$ alloys is linked to the *L* conduction band. This is verified by the study of the *DX* center in GaAs-$Ga_{1-x}Al_xAs$ superlattices, where it is observed that the *DX* center does exist only in GaAs-AlAs superlattices such that the *L* miniband which replaces the *L* band of the AlAs barrier is at the same energy as the bottom of this *L* band, although the *X* conduction band has been replaced by a Γ miniband. This property can only find an explanation in the effective-mass approximation and cannot be justified in large–lattice-relaxation models. Within this model the *DX* level is the effective-mass state of the doping impurity associated with the *L* band which undergoes a shallow-deep instability due to intervalley mixing. This description implies a small, if any, electron-phonon interaction. From our electron-paramagnetic-resonance studies we conclude that the large threshold for optical ionization involves a transition to a higher state than the bottom of the conduction band and must probably be attributed to an internal transition. The barrier for electron capture is explained as originating from a change of the local force constants of the defect with its charge state. The variation of the capture barrier height with alloy composition is quantitatively accounted for by electron emission from the bottom of the conduction band into the *L* band, followed by a multiphonon-emission process over a constant barrier.

I. INTRODUCTION

There have been several attempts to explain the properties of the *DX* center in $Ga_xAl_{1-x}As$ alloys (for a review, see Ref. 1) and, sometimes, a specific defect configuration has been proposed to account for these characteristics. The *DX*-center-associated energy level is resonant in GaAs (Ref. 2) and becomes localized when the alloy composition (AlAs mole fraction) x is larger than ~ 0.2 (or, equivalently, under sufficient hydrostatic pressure). This level, E_T, appears to follow the *L* band[3] and, thus, its location relative to the bottom of the conduction band varies with x. There is a barrier E_C for electron trapping,[4] also varying with x, which is such that the ionization energy, $E_i = E_C + E_T$, as measured by deep-level transient spectroscopy (DLTS), the technique used to detect quantitatively the defect, is constant. As the apparent optical ionization energy E_0 is large compared to E_T,[5] a larger electron-phonon interaction (i.e., a large lattice relaxation or distortion) is usually assumed.

Because the concentration of the *DX* center is proportional and close to the donor impurity concentration,[1] the *DX* center was first thought to be a complex between the donor *D* and an unknown defect *X*.[1] Unfortunately, it is difficult to accept that the concentration of *X* can be as high as $\sim 10^{19}$ cm^{-3}, the *DX* concentration in a 10^{19}–cm^{-3} doped material, and not detected in a material doped with $\sim 10^{16}$ cm^{-3} impurities which contains only $\sim 10^{16}$ cm^{-3} *DX* centers. For other reasons, such as the fact that H passivates *D* and *DX* at the same time and with similar kinetics,[6] and the existance of the *DX* centers in doped GaAs submitted to hyrostatic pressure, it has been suggested that *DX* is *D* itself. This suggestion cannot be verified directly using electrical techniques because all the free carriers are trapped on E_T when the *DX* centers are filled and the material is semi-insulating. However, the fact that the free-carrier and the *DX* concentrations are equal can be demonstrated[7] by an examination of the trapping kinetics which take a very peculiar shape[8] when the equality is fulfilled.

II. LARGE OR SMALL LATTICE RELAXATION?

Models of *DX* centers involving large lattice distortion or relaxation have been proposed[9–11] in order to account for the deepening of the energy level associated with the doping impurity (whose energy level is in principle shallow), as well as to explain the existence of E_C and of the strong electron-phonon interaction revealed by the large difference between E_0 and E_T. For instance, Morgan[10] assumes a large Jahn-Teller distortion. Large lattice distortion is, of course, also implied in models involving a negative-U character[9,12]. However, when a defect induces a strong displacement of the neighboring atoms, its associated wave function has to be built with all atomic orbitals in interaction, the orbitals of the impurity and of the displaced neighboring atoms. In no way can all these states originate from one single particular conduction band (antibonding states). In this case, it can only be accidental that a defect, here the *DX* center, is apparently linked to a particular (*L*) conduction band. Consequently, the question of knowing if the *DX* center is really linked to the *L* band is crucial to distinguishing between small- and large–lattice-relaxation models. It has often been stated using various observations that the *DX* level is linked to the *L* band because the variation of E_T versus x was found to be nearly identical to those of *L*, but this is not a sufficient argument, as we shall see below. A correct argument comes, as shown in Sec. III, from a systematic study of the capture barrier E_C versus x and hydrostatic pressure.[3] We shall see that the variation of the capture barrier E_C versus x implies that electrons have first to occupy the *L* band before they can recombine on *DX* centers, thus demonstrating unambiguously that the *DX* level must indeed be linked to his band. A verification has been performed in Sec. V by using GaAs-$\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ and GaAs-AlAs superlattices in which it is possible to change the nature and energetical position of the various bands: only when the *L* band of the barriers is replaced by an *L* miniband at the same energy location is the *DX* center present, even when the nature of the lowest conduction band has been changed.

Chadi and Chang[9] argue that the *DX* level is not linked to the *L* band but, as is every deep level, to the Brillouin-zone–average energy of the conduction band. Because this average energy varies with x approximately like the *L* band, it is difficult to distinguish between the two cases only from the variation of the thermal ionization energy (they thus ignore the decisive argument provided by the variation of E_C versus x. However, first, the *DX* level is not a usual deep state since, depending on the x value, it is also a resonant state (for $x<0.2$) or a shallow state (for $x\sim 0.2-0.3$). Second, the assumption that any deep state follows the Brillouin-zone–average energy of the conduction band, i.e., is such that $\Delta E_T=\alpha\Delta x$, with $\alpha=(0.55\ \mathrm{eV})x^{-1}$, is not justified. It can only apply to defects whose wave functions are described exclusively in terms of antibonding states; i.e., donor states which are not distorted. Indeed a defect involving a lattice distortion has a wave function which is also built with valence-band states. This is easily verified experimentally: donor or acceptor states do not follow the conduction or the valence bands, respectively. For instance, in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$, the defect labeled $E3$, an intrinsic defect created by electron irradiation and attributed to an As vacancy perturbed by a nearby As interstitial,[13] has an energy level deeper than the *DX* level which remains linked[14] to the valence band as x varies, i.e., $\alpha(E3)=0$. For defects such as native ones (labeled *A* and *B*, present in liquid-phase-epitaxy materials) and Cu- and Fe-related ones, $\alpha\simeq 0.4$.[14] For the $E1,E2$ levels[14] also introduced by electron irradiation[13] $\alpha(E1,E2)\simeq 1$. Thus α can take values having a rather wide range and there is no unique value associated with deep levels. In GaAs under pressure, the $E2$, $E3$, and $E4$ levels shift markedly away from the conduction minimum with pressure and there is no apparent relationship, for any of them, between their position in the gap and their dependence on pressure.[15] Strongly different pressure coefficients are always found in GaAs for various native traps.[16] Actually, as shown by Ren *et al.*,[17] the pressure derivative of a level associated with a substitution impurity varies with the level depth in a way which depends on the site and on the symmetry. In conclusion, the argument used by Chadi and Chang that the deep level associated with their defect model should follow the conduction-band average energy is not substantiated and should not be used as proof of the validity of their model.

III. THE MODEL

The first consequence of the fact that the *DX*-center-associated level is linked to a particular band is that it must be described in terms of the effective-mass theory. Indeed, for a deep level, i.e. for a defect associated with a short-range potential, even when it can be described in terms of the wave function of one particular band, the associated level will not be linked to this band. This important point can be simply demonstrated. For this we consider a defect whose wave function ψ can be described in terms of a linear combination of the wave functions ψ_k of a particular band:

$$\psi=\sum_k a_k\psi_k \ .$$

The Hamiltonian of the crystal containing the defect can be written as the sum of the Hamiltonian H_0 of the perfect crystal and of the potential V induced by the defect:

$$H=H_0+V \ .$$

Using the description, the defect state being

$$\langle\psi|H|\psi\rangle=\sum_{k,k'}a_k a_{k'}\langle\psi_k|(H_0+V)|\psi_{k'}\rangle \ ,$$

its change with alloy composition x (or equivalently with hydrostatic pressure) $(\partial\partial x)$ $\langle\psi|H|\psi\rangle$ is composed of three terms:

$$\sum_{k,k'}a_k a_{k'}\frac{\partial}{\partial x}\langle\psi_k|H_0|\psi_{k'}\rangle \ ,$$

$$\sum_{k,k'}a_k a_{k'}\frac{\partial}{\partial x}\langle\psi_k|V|\psi_{k'}\rangle \ ,$$

and

$$\sum_{k,k'}\left[a_k\frac{\partial a_k}{\partial x}+a_k\frac{\partial a_{k'}}{\partial x}\right](\langle\psi_k|H_0|\psi_{k'}\rangle+\langle\psi_k|V|\psi_{k'}\rangle) \ .$$

Thus the change versus x of the defect state is equal to the band-state change

$$\sum_{k,k'}\frac{\partial}{\partial x}\langle\psi_k|H_0|\psi_{k'}\rangle$$

(i.e., the defect level is linked to the band) only when

$$\frac{\partial a}{\partial x}=0$$

and

$$\sum_{k,k'}\frac{\partial}{\partial x}\langle\psi_k|V|\psi_{k'}\rangle=0 \ .$$

This can only occur when the potential V does not depend on x, i.e., when it is produced by a point charge, independently of its position in the lattice. This potential is a (screened) Coulomb potential which then obliges us to treat the electronic state of the defect in the effective-mass approximation. However, the energy variations of the level and of the band versus x are not exactly equal since the effective mass is x dependent. Consequently, the fact that the energy level follows exactly the variation of the band is not a good criterion to decide if it is linked to it.

The only way to describe a defect-associated wave function in order to get an associated energy level E_T^L linked to a particular band (L) is to use the effective-mass approximation. Nevertheless, for the *DX* center, because E_T^L is not shallow like a pure effective-mass state should be, one must introduce in the effective-mass description a kind of central-cell correction. In the case of the L conduction band of GaAs the physical origin of this correction is obvious; it is the mixing between the four equivalent valleys. This model was suggested several times[18,19] and substantiated to some extent by photoluminescence studies.[20–22] The numerical treatment, demonstrating that the L effective-mass state can indeed undergo a shallow-deep instability, has only been recently performed.[23] This treatment is not, however, capable of providing the exact value of E_T^L because the ionization energy depends critically on the extension in space R (~ 1 Å) for which the Bloch functions at the minima of the four valleys remain coherent. But, when one takes for R the value (1.7 atomic units) corresponding to the experimental ionization energy ($E_T^L = 0.16$ eV for Si), we obtain as expected a strongly localized wave function (see Fig. 1).

Thus, the picture in which the *DX* state is nothing but the L-band effective-mass state of the doping impurity, deepened by a particular band-structure effect, namely intervalley mixing, is the only one able to account correctly for the fact that the *DX* level is linked to the L band. From this model it follows directly that the concentrations of the *DX* centers and of the doping impurities are equal, explaining the particular type of trapping kinetics observed.[7,8] However, this model implies a small lattice relaxation which is *a priori* in contradiction with the large difference between the threshold for the optical cross section E_0 and the thermal ionization energy E_T and with the existence of the barrier E_C associated with the electron-capture cross section. These contradictions, however, can be raised as we shall now discuss.

First, we shall demonstrate experimentally in Sec. VI that the optical transition does not correspond to a transition between E_T and the Γ or L band and we argue that it is related to an internal, such as an $A_1 \rightarrow T_2$, transition. For such an A_1-T_2 transition the energy expected is on the order of 1 eV, as experimentally observed.[5] The optical spectrum associated with this transition is similar to a photoionization spectrum because the excited states are distributed into a broad band due to electron-phonon coupling and the interaction with the conduction-band states. Photoionization into the Γ, L, and X bands perhaps appears as shoulders on the edge of the spectrum.[22] But practically no study has been performed below 0.5 eV. As noted by Henning and Ansems, at photon energies lower than typically 0.5 eV, free-carrier absorption becomes large and tends to overrule the photoionization, thus allowing us to understand that these transitions are difficult to observe. As we shall see in Sec. VI, electron paramagnetic resonance (EPR) clearly shows that the photoionization involves a band higher than the Γ and L bands.

The existence of a barrier E_C for the capture of an electron on the *DX* level can be understood in the following way. The local force constant k, describing the defect vibrational energy

$$E = \tfrac{1}{2} k Q^2$$

versus a particular configuration coordinate Q, is charge-state dependent. A variation from k to k' when an electron (in the L band) gets trapped on the defect (see Fig. 2)

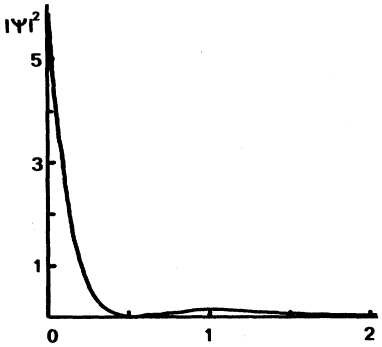

FIG. 1. Extension in space, R (in atomic units), of the density of probability $|\psi|^2$ of the normalized wave function ψ calculated for a value of the parameter $R = 1.742$ a.u. corresponding to the binding energy of 160 meV (Si); ψ is a $2S$ function, with $|\psi|^2 = 0$ for $R \sim 0.5$ a.u. $|\psi|^2$ decreases exponentially for large R values (verified in the range 2–16 a.u.).

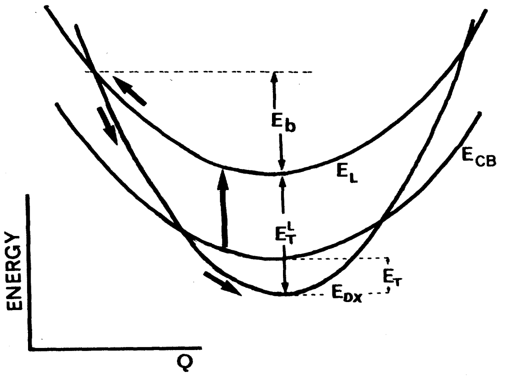

FIG. 2. Configuration coordinate diagram of the *DX* center. Curve E_{DX} corresponds to the filled state, E_L and E_{CB} to the ionized state with the electron in the L band and in the bottom of the conduction band (Γ or X, depending on x), respectively. The arrows indicate the process for electron capture.

changes the total energy to

$$E' = \tfrac{1}{2}k'Q^2 - E_T^L .$$

A barrier E_b, corresponding to the energy difference between the minimum of the total defect energy E (when the electron is in the L conduction band) and the energy at which the total energies $E(Q)$ and $E'(Q)$ cross, results, if k' is larger than k, i.e., if the occupation of the DX center by one electron leads to a stronger binding:

$$E_b = E_T^L \left[\frac{k'}{k} - 1 \right]^{-1} .$$

This picture implies a constant barrier for the capture through multiphonon emission from the L band, which is experimentally verified as we shall now see. The DX ionization energy $E_i = E_T + E_C$ remains constant[24] as x varies, while E_T is linked to the L band. The apparent capture barrier E_C, as measured by DLTS, is therefore the sum of E_b and of the energy difference Δ_{LC} between the L minimum and the bottom of the conduction band $E_i = E_T + E_b + \Delta_{LC}$. As shown in Fig. 3, the variation of $E_C = E_b + \Delta_{LC}$ with alloy composition is quantitatively reproduced taking $E_b = 200$ meV. Thus, the apparent variation of E_C versus x must be ascribed to the fact that the electrons have to occupy the L band before they can recombine. From this value of E_b and with $E_T = 0.16$ eV (the case of Si), one deduces $k'/k = 1.8$. Finally, this variation of E_C versus x, because it can only be understood if an electron has to occupy the L band before it recombines on the DX level, thus provides the first clear experimental evidence that the DX center is linked to this band.

That the origin of the DX center is a purely band-structure effect also agrees with the fact that it is present independently of the nature of the donor impurity and of its location (on Ga or As sites). A deep defect involving large lattice relaxation is expected to present characteristics strongly dependent on the impurity size and type of orbitals, i.e., on the nature of the impurity. Large–lattice-relaxation models, in order to have some chance to be valid, must first demonstrate that they can provide very similar energy levels for the various donor impurities located either on Ga or As sites.

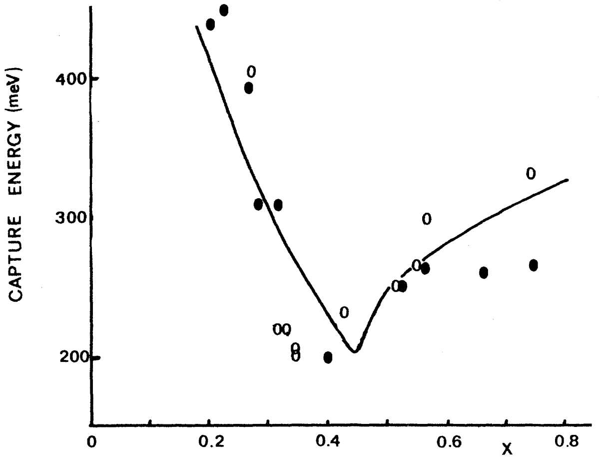

FIG. 3. Variation of the capture barrier E_C with x. The solid and empty circles indicate the experimental data of Refs. 3 and 4, respectively. The solid line corresponds to the sum of the capture barrier E_b (200 meV for Si) and of the energy difference between the L band and the bottom of the conduction band.

The existence of the shallow-deep instability is a function of R, of the electron effective mass, and of the number of valleys. The occurrence of DX centers can therefore be predicted to take place also for the X band (which contains three valleys), for other impurities,[25] and for other III-V compounds. Indications of the existence of DX centers have been found in the case of $\mathrm{Ga}_x\mathrm{As}_{1-x}\mathrm{P}$ alloys[26,27] and probably in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$,[28] $\mathrm{In}_x\mathrm{Ga}_y\mathrm{Al}_{1-x-y}\mathrm{P}$,[28] $\mathrm{In}_x\mathrm{Al}_{1-x}\mathrm{As}$,[29] $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{Sb}$,[30] and $\mathrm{In}_x\mathrm{Ga}_y\mathrm{Al}_{1-x-y}\mathrm{P}$ (Ref. 31) as well.

IV. THE ALLOYING EFFECT

Several observations made on the DX center are interpreted in terms of a so-called alloying effect, i.e., of the influence of the nature of the neighboring atoms, which is not unique for a given alloy composition. When the defect potential is a long-range Coulomb potential, this effect should be negligible because the effective-mass model is insensitive to the local fluctuations of the neighbors and depends only on the long-range part of the potential. However, in case of a shallow-deep instability it is the short-range part of the potential which can become important and alloying effects could indeed occur. This question will therefore now be discussed.

It is often argued that alloying effects are revealed in the capture kinetics, the emission kinetics, and in the shape of the peak provided by deep-level transient spectroscopy. The capture kinetics, systematically studied by Mooney *et al.*,[4] exhibit a broad distribution of capture time constants that these authors ascribe to a distribution of capture barrier heights. They fitted the observed kinetics with a Gaussian distribution of capture barriers whose width depends on alloy composition. However, as demonstrated in Refs. 7 and 8, this distribution of time constants is a natural consequence of the fact that the DX concentration is equal to the doping impurity concentration. The capture kinetics can be fitted using a single capture time constant, i.e., using a single barrier height when the material is nondegenerate. There is therefore no evidence of an alloying effect. Mooney *et al*[4] used kinetics involving three fitting parameters, thus introducing the alloying effect, arguing that they could not fit the kinetics for the case of highly degenerate materials. However, that a simple bimolecular kinetics does not apply in this case is the result of the variation of Δ_{LC} with the filling level in the degenerate band.

The emission kinetics are also nonexponential and this has again been attributed to alloy broadening.[32] However, several other reasons can equally explain this nonexponential behavior. One is the fact that the capture cross section being exponentially activated, the filling factor of the DX center (during the application of the DLTS pulse) varies strongly with temperature. Since this variation occurs in the same temperature range where emission takes place, this results in a strong distortion of the DLTS peak.[8] Even in the case where the kinetics is monitored after the application of one single pulse, i.e. at constant temperature, the nonexponentiality is induced when the pulse width is long enough to fill a large fraction of the *DX* centers because then the free-carrier concentration is not large compared to *DX* concentration and the space-charge region varies as the emission proceeds.[33]

A third observation often put forward in favor of the alloying effect is that the *DX* spectrum exhibits a fine structure.[34–38] Up to three components are revealed (see Fig. 4) in the shape of the DLTS peak and not only in the case of small x values. The existence of a small number of well-defined components is, however, in contradiction with the existence of a Gaussian distribution of capture barriers. Schematically, the DLTS peak can be decomposed into three components whose relative amplitudes vary with x. These components have different ionization energies and capture cross sections, as revealed by the variation of the relative amplitudes versus the filling pulse (Fig. 4). Unfortunately, the decomposition of the spectrum in three components should be invariant for a given value of x, which is not the case. As we shall develop elsewhere, the shape of the spectrum can be dependent on the thickness of the layer in molecular-beam epitaxy (MBE) materials and this spectrum contains only one component in liquid-phase-epitaxy (LPE) layers grown on thick $Ga_{1-x}Al_xAs$ layers. For these reasons we attribute the change in spectrum shape to a strain effect. A strain is expected to lift the degeneracy of the four L valleys and to give rise to several components in the *DX* spectrum. Finally, we have shown that the capture process occurs by the sequential jumps of an electron from the bottom of the lowest conduction band (Γ or X, depending on x) into the L band and then over the barrier E_b into *DX*. When two or three of the bands are not too far separated in energy, they can be occupied by the emitted electrons, giving rise to three distinct emission rates. The relative amplitudes of the peaks are not a simple function of the probabilities of ionization in the different bands because the capture cross section varies rapidly with the temperature in the temperature range where the DLTS spectrum is recorded. This is illustrated in Fig. 4 where it can be seen that the relative amplitudes of the three components vary with the filling time. A detailed justification will be described elsewhere.

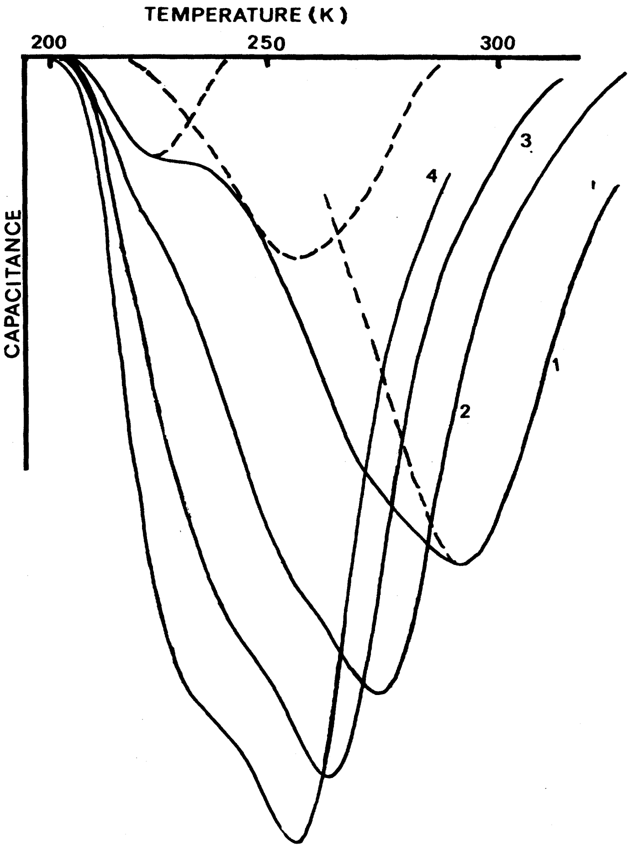

FIG. 4. Variation of the DLTS peak shape of the *DX* center for $x=0.3$, made of three components (dashed lines), vs filling time (1, 0.5 ms; 2, 2 ms; 3, 5 ms; 4, 10 ms).

V. EXPERIMENTAL VERIFICATION

How can we get additional experimental evidence that the *DX* level is linked to the L band and thus that this effective-mass model is the right one? This can be done by introducing doping impurities in $Ga_{1-x}Al_xAs$ layers, in such a way that the local environment of the impurity is identical to the one it has in bulk material, and to pile them in a periodic GaAs-$Ga_{1-x}Al_xAs$ heterostructure which will change the band structure of $Ga_{1-x}Al_xAs$, thus modifying the energy of the L band responsible for the occurrence of the *DX* level. The type of heterostructure having a modified band structure is a superlattice in which the electron tunnels through the barriers, giving rise to a series of minibands in the direction perpendicular to the layers. Because the electronic density is homogeneous in this direction the superlattice can be placed in the space-charge region of a Schottky barrier, with the electric field perpendicular to the layers, and DLTS can be applied[39] as on a bulk material. This allows us to detect defects[40] and in particular the *DX* center, if present. The DLTS peaks then relect the transition of an electron from the localized level to the bottom of the first miniband.[41] Measurements have been performed on a series of uniformly Si-doped ($\sim 10^{16}$ cm^{-3}) GaAs-$Ga_{1-x}Al_xAs$ periodic structures (for $x=0.3$) having the following well-barrier widths: (20 Å)/(20 Å), (30 Å)/(30 Å), (40 Å)/(40 Å), (40 Å)/(20 Å), and (50 Å)/(50 Å). No DLTS spectrum is detected in the range 4–300 K except in the (40 Å)/(20 Å) and (50 Å)/(50 Å) structures. The spectrum, which has an amplitude large enough to allow its analysis only in the (50 Å)/(50 Å) structure, exhibits a rich structure including a peak having the same shape and an identical signature (emission rate versus temperature) as the *DX* center in bulk $Ga_{1-x}Al_xAs$ (see Fig. 5). The full analysis of this structure is presented elsewhere[42]

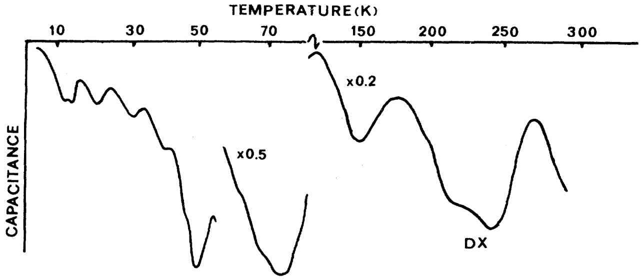

FIG. 5. DLTS spectrum observed in a (50 Å)/(50 Å) structure indicating the peak associated with the *DX* center (emission rate 213 s^{-1}, reverse bias 2V, pulse amplitude 1 V, pulse width 0.5 ms). The variation of the emission rate vs the inverse of the temperature provides an ionization energy of 0.42 eV.

and we concentrate here on the *DX* associated peak. The reason the *DX* center has the same ionization energy as in the bulk material is due to the fact that the electric field F in the space-charge region has induced the localization of the electronic density[42] in the wells, the quantity eFd (where d is the superlattice period) being larger than the width of the miniband. This effect is only clearly observed, at least with the conditions used, namely reverse bias voltages up to 3 V over typically 1 μm, in the (50 Å)/(50 Å) structure because the width of the miniband is smaller (8 meV) than in the other structures (200–25 meV). This result demonstrates therefore that (i) *DX* centers exist in $Ga_{1-x}Al_xAs$ barriers when the original band structure is preserved (when the electric field induces the localization) and they can be detected and (ii) *DX* centers are not detected at the energy position they should occupy when the structures behave as superlattices. However, the nonexistence of the *DX* centers in these superlattices can also be inferred by the fact that the *DX* associated level ($\sim$0.16 eV below the bottom of the $Ga_{1-x}Al_xAs$ conduction band for Si) could be located above the minimum of the first miniband (the band offset being 0.28 eV, the calculated minima of the bottoms of the minibands are located in the range 150–200 meV below the bottom of the $Ga_{1-x}Al_xAs$ conduction band).

To put clearly in evidence the expected band-structure effect, one has to consider a superlattice in which the *DX* level will clearly not be resonant. This can be done using periodic planar doping in $Ga_{1-x}Al_xAs$ since then, the doping impurities being located in the doped planes, the *DX* level is always below the bottom of the well and thus can never be resonant. When the doping concentration n per plane is low enough, the depth of the wells is small (typically $\sim$ 50 meV for $n = 10^{12}$ cm^{-2}) and induces only a small perturbation on the original band structure, and the *DX* centers should be present. However, as soon as n becomes large enough, the well depth increases (it is of the order of 600 meV for $n = 3\times10^{13}$ cm^{-2}), modifying the band structure in the direction perpendicular to the planes, and the *DX* center should disappear. This is actually what is observed experimentally: as shown by Etienne and Thierry-Mieg[43] the *DX* center is present for low doping but its concentration drops down abruptly to zero for n of the order of 2×10^{13} cm^{-2} (in which case the first subband is expected to be at about 200 meV above the bottom of the well).

This can also be done using GaAs-AlAs short-period superlattices because then the X band of the AlAs barriers can be replaced by a Γ miniband whose energetical position relative to the bottom of the X band can be varied while the L miniband remains at the same position as the bottom of the L band. In Si-doped (3×10^{16} cm^{-3}) (35 Å)/(17 Å) well-barrier width GaAs-AlAs superlattices we have detected[44] the *DX* center whose DLTS spectra are identical to the ones found in $Ga_{1-x}Al_xAs$ and AlAs layers. Because in these two superlattices the Γ miniband positions are different but the L minibands remain within 10 meV at the position of the bottom of the L conduction band in AlAs, this demonstrates that the *DX* level is independent of the nature and position of the lowest conduction band (implying that electron emission occurs directly in the L band and not, as usually assumed, into the bottom of the conduction band) and, again, that it is linked to the L miniband.

In conclusion, the results obtained with these superlattices verify the conclusion drawn from the variation of E_C versus x, namely that the *DX* level is linked to the L band. Thus in order to be fully satisfied by the effective-mass model, it remains to understand the apparent behavior of the photoionization process, i.e. the fact that E_0 is larger than E_T (or E_T^L). This is done in the next section.

VI. DETECTION BY ELECTRON PARAMAGNETIC RESONANCE

Single donors, effective-mass-like or deep, are expected to be paramagnetic in their neutral charge state and should then be observable by EPR. The EPR spectrum gives information on the wave-function extension as well as on the presence of a local lattice relaxation lowering the point symmetry of the lattice site. The EPR spectra of both the effective-mass donors, linked to the Γ band in GaAs and to the X band in $Ga_{1-x}Al_xAs$ (for $x > 0.45$), have been observed.[45,46] The deep donor *DX* is in principle also expected to have a paramagnetic ground state. However, no EPR spectrum associated with *DX* has been observed up to now. We have studied sufficiently thick samples of Sn-doped $Ga_{1-x}Al_xAs$ ($x = 0.3$) grown by the metalorganic vapor-phase epitaxy technique. The sample characteristics (thickness, 30 μm; doping concentration, 10^{18} cm^{-3}) are such that the number of spins, assumed to be equal to that of the *DX* center, should allow their detection in an X-band spectrometer. The results can be summarized as follows:[47] When the sample has been cooled down in thermal equilibrium no EPR spectrum is observed. Under photoexcitation with an energy larger than 0.8 eV, a metastable paramagnetic spectrum is observed with a g factor of 1.95 characteristic of an X-related donor state. This excited state is separated from the ground state by a thermal barrier of $\sim$10 meV estimated from its kinetics of decrease versus temperature. As to the photoexcitation spectrum of this defect, it is similar to the photoionization spectrum of the *DX* center associated with the Sn impurity as determined by photocapacitance spectroscopy. These results, which are detailed elsewhere,[47] thus demonstrate (i) the existence of a metastable *X*-related state associated with the *DX* center and (ii) that the photoionization involves a transition higher than the transition into the *L* conduction band.

Then why is the photoionization towards the bottom of the conduction band not observed? First, since the defect wave function is a purely *L* state, the optical transition should occur towards the *L* band and not towards the Γ or *X* bottom of the conduction band (a conclusion in agreement with the fact that, as shown in the preceding section, thermal ionization occurs directly in the *L* band). If the optical excitation which is necessary to induce the *DX*−*L*-band transition is also able to excite free electrons over the barrier E_b, resulting in its capture by the *DX* center, then the net result will be the nonobservation of the photoionization process.

Finally, the nonobservation by EPR of the *DX* ground state could be due to excessive linewidth effects.

VII. CONCLUSION

In conclusion, the results obtained with the superlattices show unambiguously that the *DX* center is suppressed by a modification of the band structure, as expected in the effective-mass model. They also demonstrate, together with the variation of the capture barrier height versus *x*, that the *DX* level is linked to the *L* band, a fact which implies that the *DX* center is the *L* effective-mass state of the doping impurity, deepened by intervalley mixing. It is accompanied by small, if any, lattice distortion or relaxation effects, since otherwise the *DX* level would not be linked to the *L* band. We have shown that this model can reconcile all existing data, reasonably well including the existence of a large photoionization process.

Finally, we mention briefly a direct confirmation of this conclusion described in detail elsewhere[48] which is not directly dependent on the nature of the wave function since it deals with the defect potential. We have found in Te-doped LPE material (for $x=0.25$) that the thermal ionization energy E_i is enhanced by the electric field present in the space-charge region. This enhancement fits the Poole-Frenkel effect for a single donor. This means that the defect is a single donor, as are the shallow effective-mass states associated with the Γ and *X* bands, and that the binding potential is a Coulomb one. This is the expected result for an effective-mass state and, once again, in contradiction with any deep defect model. The fact that two different levels associated with the same impurity give rise to two independent singly charged donor levels can only be understood if they arise from two effective-mass states of two different bands.

This conclusion is important from a technological point of view since it tells how this center can be suppressed.[49] It also allows us to understand how the limitation of the free-carrier concentration which occurs with heavy doping in GaAs can be overcome. Free carriers are produced as long as the Fermi level does not reach the (resonant in GaAs) *DX* level. When this happens all additional free carriers fill the *DX* centers and the Fermi level remains frozen on its level. This limitation no longer exists in a superlattice or in the case of planar doping, thus explaining that higher effective doping concentrations can then be achieved.[50]

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