PHYSICAL REVIEW B VOLUME 41, NUMBER 12 15 APRIL 1990-II

Energy level associated with the *DX* center in $Ga_{1-x}Al_xAs$

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(Received 8 September 1989)

We examine in detail the variation of the *DX*-associated energy-level position versus alloy composition. It is found to be located at a constant energy from the *L* band whatever the nature of the impurity and the lattice site it occupies. Using the enhancement of the electron emission rate from the *DX* center with electric field, which happens to be characteristic of a Poole-Frenkel effect, we deduce that this energy level corresponds to a single donor state. The existence in the gap of two single donor levels, one shallow and one deep associated with the *DX* center, implies that these levels must arise from two effective-mass states associated with two different conduction bands: the shallow one with the lowest conduction band, and the deep one with the *L* band. We develop the statistics of occupation corresponding to this unusual situation. The identification of the *DX* level with the *L* effective-mass state deepened by intervalley mixing is in agreement with the Coulombic nature of its potential.

I. INTRODUCTION

The *DX* center is a deep level which is introduced in $Ga_{1-x}Al_xAs$ layers when it is doped with an *n*-type impurity such as Si,Sn,S,Se,Te (for a review see Ref. 1). Because its concentration is of the same order of magnitude as the doping concentration and because its kinetics for H passivation and depassivation is practically identical to the one of the doping impurity,[2-4] it is now admitted that this defect is directly related to the isolated doping impurity. Today, there are basically two opposite models that are proposed to account for the existence of this center. The first one, based on the existence of an energetic barrier (E_c) for electron capture and on a threshold energy for optical ionization (E_0) large compared to the thermal ionization energy (E_i), postulates the existence of a large-lattice distortion around the impurity; it is the so-called large-lattice-relaxation (LLR) model (for a review see Ref. 5). The second one, on the contrary, states that the *DX* center is nothing but the *L* effective-mass state of the doping impurity which undergoes a shallow-deep instability due to intervalley mixing.[6-8] Within this last model, the so-called small-lattice-relaxation (SLR) model, the capture barrier E_c is a consequence of the fact that the electron has to be in the *L* band in order to recombine,[9] with an eventual change of the local force constant of the center when it traps an electron.[10] The optical transition observed does not correspond to the ionization into the bottom of the conduction band but is an internal transition.[9] This assumption, in agreement with the fact that the threshold energy of this transition does not depend on the alloy composition, i.e., on the band structure, is strongly supported by recent electron paramagnetic resonance observations[11] and allows us to understand luminescence data.[12]

The central point, which should allow us to decide which model applies, is the fact that the *DX* level is linked or not linked to the *L* band. Indeed, a defect wave function is built from the states belonging to one single band only in the case of an effective-mass state, even when it is deepened by some kind of central-cell correction. On the contrary a deep level, especially when accompanied by a large-lattice distortion of the surrounding atoms, possesses a wave function built on several types of conduction- and valence-band states and thus is not linked to a particular band.

For an effective-mass state we expect that the location of the associated level E_{DX} in the forbidden gap (below the bottom of the conduction band) will be to first-order independent on the nature of the impurity. In the case of the existence of a shallow-deep instability due to intervalley mixing, it is reasonable to think that other types of central-cell corrections will be small compared to the correction introduced by this mixing. In addition, an effective-mass state is characterized by a Coulomb potential which can be distinguished from the short-range potential of a deep defect by looking at the variation of the electron emission rate versus the amplitude of an electric field. Finally, in the effective-mass model there are two effective-mass single donor states in the gap whose levels are associated with the doping impurity: the deep one originating from the *L* band and the shallow one for the lowest (Γ or *X*) conduction band. On the contrary, in the case of the LLR model only one of the impurity-associated level can be a single donor, i.e., be neutral when filled with an electron. Thus another way to distinguish between the two models is to look at the possible donor nature of the *DX* level.

The aim of the communication is to examine in detail these questions: donor nature of the *DX* level, extension in space of its potential, and impurity effect on the level position. For this, we start from the fact that there are indeed one shallow effective-mass level and one deep level (the *DX* center) in *n*-type doped $Ga_{1-x}Al_xAs$. We first demonstrate that the *DX* center is also a single donor level as is the shallow effective-mass level and that it is associated with a Coulomb potential. Then, we consider the energetic location of the *DX* center in the gap versus the alloy composition x for the different impurities. For this we shall compile the data previously published for the various impurities (mostly for Si, Sn, Se, S, and Te) only adding new data for an x value for which the *DX* center has not yet been observed, namely, $x=1$ (Si-doped AlAs).

We shall see that, within the experimental accuracy, all the impurities, whatever their chemical nature and the lattice site (As or Ga) they occupy, give rise to the same level location, which remains at a constant energy from the L band.

A critical examination of all this results together with the fact that the impurity gives rise to two different single donor states, allows us to deduce that the *DX* level cannot be a deep state but must originate from an effective-mass state associated with the L band, in agreement with the SLR model. We finally develop the statistics of occupation of the *DX* level since the situation of two single donor states related to only one impurity has not been considered yet.

II. THE DONOR NATURE OF THE DX CENTER

There are two levels, in concentrations similar to the doping concentration, in n-type doped $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$. One is the shallow effective-mass state E_S at a few meV below the conduction band (Γ or X depending on the alloy composition x). The other one is the *DX* center E_{DX}. The existence of E_S is provided by several observations: first, in GaAs where the *DX* level is present but resonant above the Γ band,[13] the doping impurity obviously produces a Γ effective-mass state. Second, luminescence studies in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ (Ref. 14), which detect several donor acceptor-pair transitions, clearly indicate the presence of shallow donor effective-mass states as does the temperature variation of the free-carrier concentration at low temperature in direct or indirect band gap alloys.

In order to look for the nature of the *DX* state, we have investigated the electric-field dependence of the thermal electron emission rate from the *DX* center. Indeed, when this emission rate is enhanced by a Poole-Frenkel effect, one can then deduce that the defect potential is a Coulomb one, attractive for the electron, i.e., that the defect is a donor. This is actually what happens in a specific case as we now describe. On the contrary, in the case of the short-range potential of a deep level, the emission rate is enhanced by phonon-assisted tunneling.

The measurement of the variation of the emission rate of an electron from the *DX* center is made using deep-level transient spectroscopy (DLTS). It is necessary to take numerous precautions because the capacitance transients can be perturbed by several effects. First, the amplitude of the transient must remain small compared to the capacitance of the space-charge region. To fulfill this condition it is necessary to fill only a small fraction of the *DX* centers, so that the ratio between the concentration of these filled centers and the free-carrier concentration remains small, thus insuring that the width of the space-charge region does not vary as the emission proceeds. This is obtained by using a filling pulse of small width (20 μs). The use of a fast capture rate allows an occupancy factor independent of the temperature in the range where the DLTS spectrum is monitored. Second, it is necessary to select the material in such a way that the DLTS spectrum is not perturbed by the existence of internal strains. Indeed, as we shall develop elsewhere, strain effects produce strong deformations of the *DX* spectrum which have been often observed[15-18] but attributed to a so-called alloying effect. We therefore selected a thin layer, 8×10^{16} cm^{-3} Te-doped $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ ($x=0.25$) grown by liquid-phase epitaxy (LPE) over a thick p^+-type $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ layer of variable alloy composition which provides the junction. We have verified that the DLTS spectrum obtained with this material has a shape undistinguishable from the theoretical one.

The *DX* ionization energy E_i is obtained by performing the measurement of the emission rate e_n versus temperature; it is the slope of $\ln(e_n,T^2)$ versus T^{-1}. The variation of E_i versus the electric field is obtained by performing this plot for different amplitudes of the filling pulse at a given reverse bias. The results are shown in Fig. 1. This way we measure the variation of the ionization energy ΔE_i versus the electric field F, which varies from 1.24×10^5 to 1.71×10^4 V cm^{-1} (for a reverse bias of 3 V), as compared to the minimum possible value of F. This variation is given in Fig. 2. Within the experimental accuracy, ΔE_i varies linearly with the square root of F as expected for a Poole-Frenkel effect. For a purely

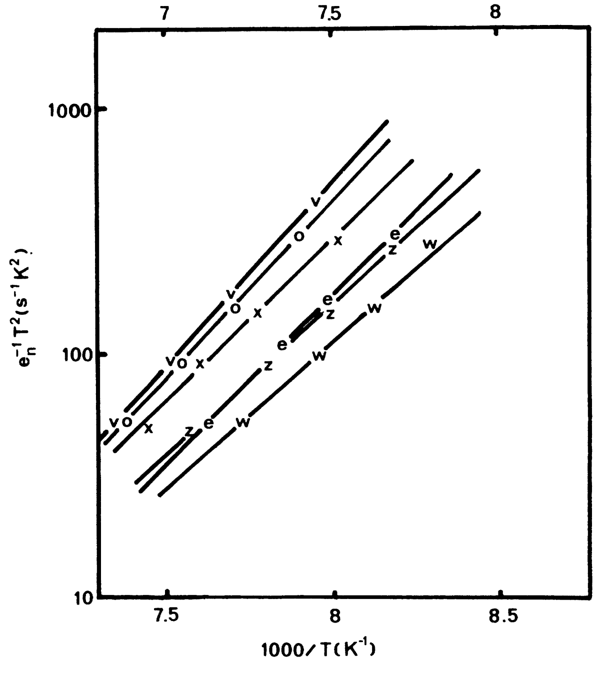

FIG. 1. Variation of the emission rate e_n vs temperature of the *DX* center in Te-doped $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ (alloy composition 0.25) for different electric fields: $V=1.7$, $O=3.5$, $X=7.6$, $e=5.5$, $Z=12.4$, and $W=9.8\times10^4$ V cm^{-1} (O,X,Z, bottom scale; V,E,W, top scale).

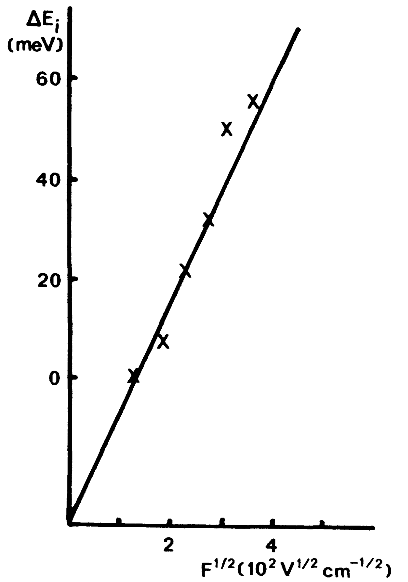

FIG. 2. Change in the ionization energy of the *DX* center, vs the square root of the electric field, as measured from the slope of the curves ln $e_n(T^{-1})$ given in Fig. 1. The origin is taken for the smallest electric field.

Coulomb field, the Poole-Frenkel effect predicts

$$\Delta E_i = q\left[\frac{qF}{\varepsilon}\right]^{1/2} . \qquad (1)$$

The theoretical coefficient $q^{3/2}/\varepsilon = 2.15\times10^{-5}$ eV $V^{-1/2}$ cm for $q=1$ is, as shown in Fig. 2, the value obtained experimentally. As we discuss elsewhere[19] the rate of enhancement versus electric field and temperature is far too small and does not exhibit the expected variation to be explained by a phonon-assisted tunneling process.

The choice of the alloy composition and of the nature of the impurity is not innocent. When the electric-field enhancement of the emission rate is investigated for other x values in Te-doped layers or for similar values in Si-doped layers, no Poole-Frenkel effect is clearly observed. The effect occurs only (i) for alloy compositions such that the L band is close in energy from the bottom of the conduction band; (ii) for impurities which exhibit a capture barrier height E_C which is equal to the energy difference Δ between the L band and the bottom of the conduction band (this is the case for Te, as we shall describe elsewhere, but not for Si for which[9] $E_C = \Delta + 200$ meV). The reason for which these conditions must be fulfilled are easily understood if we admit that the *DX* center is the effective-mass state associated with the L band.[9] Indeed, for an effective-mass state, the emission is sensitive to the Poole-Frenkel effect because it proceeds via the series of excited states close to the corresponding band, as does the capture (which takes place through the so-called cascade capture process). Thus to observe the Poole-Frenkel effect, emission has to occur directly into the L band, which implies that the L band is very close in energy from the bottom of the conduction band. Second, the cascade process occurs only if there is no barrier for the recombination for an electron in the L band. It therefore applies only for impurities for which E_C is equal to Δ, i.e., Te and not Si. Thus, a consequence of the fact that the Poole-Frenkel effect is only observed for these specific conditions is that the *DX* level is linked to the L band.

In conclusion, electron emission from the *DX* center is enhanced by the Poole-Frenkel effect when the conditions for its occurrence are fulfilled. Consequently, the *DX* center is a single donor, neutral when filled. An identical conclusion has recently been reached using magnetic susceptibility measurements.[20]

III. ENERGY-LEVEL DETERMINATION

E_{DX} is usually obtained using Hall-effect measurements through the slope E of the plot ln$n$ versus T^{-1} provided by the variation of the free-carrier concentration n versus temperature T, in the temperature range where this level is ionized (typically above 150–200 K depending on the impurity considered). The carrier concentration can equivalently be obtained from capacitance-voltage (C-V) measurements through the slope of $C^{-2}(V)$.

Depending upon the authors E_{DX} is taken as being E or $E/2$. In the case of a single donor in concentration N_D compensated by N_A acceptors, at low temperature: $n > N_A$ and $n < N_D - N_A$, and the donor level is $E_T = E/2$. However, in the case considered here, there are two donor levels (see Sec. II) the shallow one, E_S, and the deep *DX* one, E_{DX}, and it is this deep level which compensates the shallow one. Most of the electrons are frozen on the *DX* center, $n < N_A$, and the *DX* level must be taken as $E_{DX} = E$. This point will be further discussed in Sec. V.

The third technique to get E_{DX} consist of using DLTS. This technique provides the ionization energy E_i which is the sum of E_{DX} and of the capture barrier E_c. Thus, when E_c is measured independently, one obtains E_{DX} as the difference $E_i - E_c$. In addition, DLTS is also able to directly measure E_{DX} by determining the position λ in the space-charge region, of width W, at which E_{DX} crosses the Fermi level. This is done by monitoring the variation of the amplitude of the DLTS peak ΔC versus the amplitude ΔV of the filling pulse: the extrapolation of $\Delta C(\Delta V)$ to $\Delta C = 0$ provides the value of ΔV corresponding to $W - \lambda$. Results obtained this way will be described and discussed elsewhere.

Of course, since the DLTS technique is a thermal spectroscopy, the accuracy is limited and varies with the temperature at which the measurements are performed. The temperature range where the *DX* center is observed is of the order of 10 meV. However, the data reported in the literature present a large scatter (40 meV at least). This is due to the fact that, as mentioned in Sec. II, the DLTS spectrum is often distorted by several spurious effects. The new data on Te-doped LPE materials and Si-doped molecular-beam epitaxy $Ga_{1-x}Al_xAs$ and AlAs layers which are given in this paper have been obtained using the capacitance technique through C-V measurements.

As shown in Table I (Refs. 21–36), the literature pro-

TABLE I. Values in meV of the ionization energy (E_i) obtained by DLTS, energy level (E_T) obtained by Hall-effect measurements, and capture barrier height (E_C) of the *DX* center associated with the various doping impurities in $Ga_{1-x}Al_xAs$ of various alloy composition (x).

		Si					Se					Sn					Te					S		
x	E_i	E_T	E_C	Refs.	x	E_i	E_T	E_C	Refs.	x	E_i	E_T	E_C	Refs.	x	E_i	E_T	E_C	Refs.	x	E_i	E_T	E_C	Refs.
0.19	440			22	0.98	280			29															
0.23	440			22						0.23		11		32										
0.25	430	18,15		6,22,23	0.25		8.6		30															
0.26		54		24																				
0.27	440		390	22						0.28		40		32										
0.29		55		6																				
0.30	430	60		23,25	0.31		45		30	0.30	210			25										
0.32	450	85	230	6,22			6								0.32	230			34					
0.33	240		230	22						0.34		65		32										
0.35	450	108	240	6,22,26						0.35	200	160	96	26,33	0.35		123		36					
0.36		130–150		6,24	0.36		65		30	0.39		118		32	0.31		120							
0.40		130		23	0.38		119–160		30,31															
0.42	440		230	22						0.42		129		32										
0.43		146		6	0.43	280			25	0.43	280			30	0.45	280			25	0.41	280			25
0.45		150		6	0.47		157		30															
0.48		160		6						0.48		109		32	0.48		120		36					
0.50		134–105		6,23																				
0.51	450		250	22																				
0.55	440		270	22	0.56		124		30						0.55	160	35	175	35					
0.57	460		300	22																				
0.59		136		27																				
0.60		130		6	0.60		83		30	0.62		103		32	0.60		100		36					
0.70		92		6	0.63		80		30	0.70		101		32	0.65			160	26					
0.74	460		330	22,26,28	0.71		78		30						0.70		77		36					
0.79		37		24																				
0.84		76		6	0.82		19		30						0.95		46		36					
1	400	35–29		6, this work																				

vides detailed results only in the case of Si doping. There are less data reported for Se and only few for Sn, Se, S, and Te. There has been no result reported for $x=1$, presumably because it has not been possible to perform electrical measurements in AlAs layers. For this reason we studied the *DX* center in Si-doped AlAs layers. The result obtained is also given in Table I and compiled with the literature data on Figs. 3(a) and 3(b). The data reported by Saxena[37] are also included in Fig. 3(b) but not in the table since the impurity is not specified.

As shown on Fig. 3, the data for Si, Sn, and Se lie within a band which is parallel to the *L* band, within a scatter of typically 30 meV. Owing to this accuracy, the precision with which the band energies are known (specially around $x=0.45$) and their temperature dependence (the energy level E_{DX}) are located at 200±20 meV below the *L* band. Another value, 160 meV, is often proposed[5] probably on the ground that it is the maximum value of E_{DX} near $x=0.45$ where all bands cross. However, even for this *x* value, the *L* band is perhaps not at the bottom of the conduction band and the energy difference between the *L* band and the bottom of the conduction band has to be added to this value. As to the data for Te they seem to lie on a level also parallel to the *L* band but deeper (270 meV below *L*).

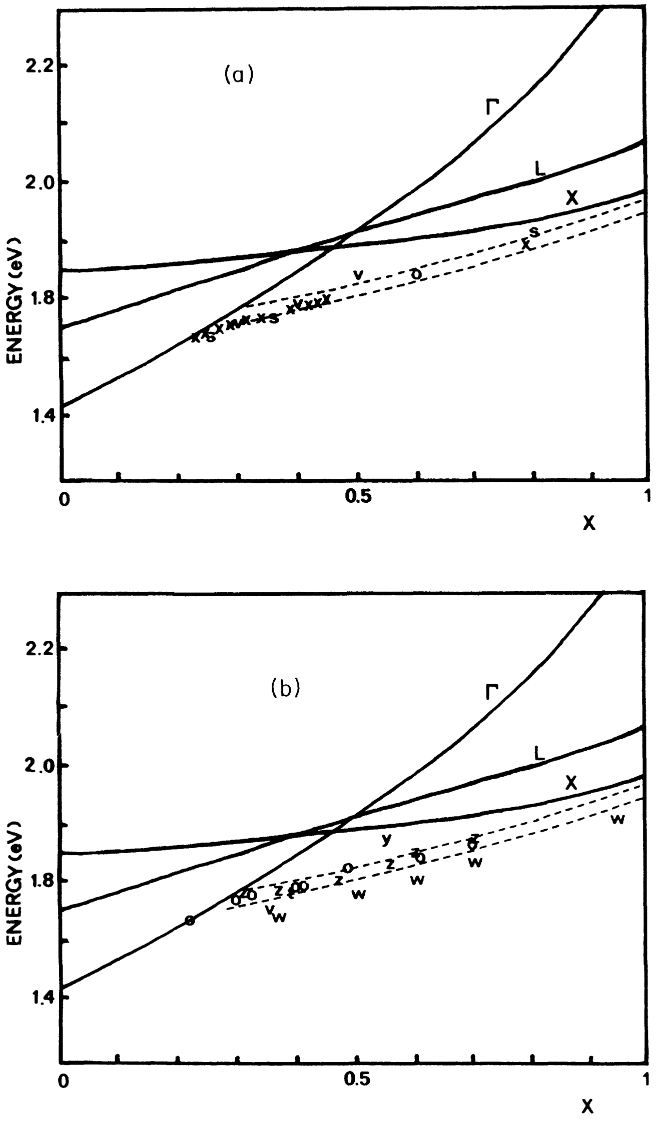

FIG. 3. (a) Energetical position of the *DX* level, as obtained from Hall-effect measurements or DLTS, in Si-doped $Ga_xAl_{1-x}As$ of variable alloy composition (*O*, Ref. 27; *S*, Ref. 21, *V*, Ref. 23; *X*, Ref. 37). The data of Ref. 6, which lie within the dashed band for the whole *x* range, are not indicated. (b) Energetical position of the *DX* level in Sn (*V*, Ref. 33; *O*, Ref. 32), Se (*Z*, Ref. 30; *t*, Ref. 31), and Te (*y*, Ref. 35; *W*, Ref. 36) -doped GaAlAs.

We can therefore conclude that, within the experimental accuracy and the precision at which the band energies are known, the energy difference between the *L* band and the *DX* level remains constant. The variations of the Γ, *L*, and *X* minima versus alloy composition we have considered are those recommended in the review article of Adachi.[38] More recent data suggest that the crossings occur at lower *x* values. However, this does not modify the conclusion, owing to the low accuracy of the experimental data. It has also been suggested from first-principle calculations[39,40] that the *L* point edge in AlAs might be considerably higher than indicated in Fig. 3. Actually, this does not seem to be the case since we observe the *DX* center in Si-doped AlAs (Ref. 41) with always the same associated activation energy.

IV. DISCUSSION

The fact that all impurities, which differ considerably by their ionic radii and which lie on one or the other of the two, As and Ga, lattice sites, give rise to a very similar (within 30 meV), if not equal, energy levels strongly suggests that their electronic states should be described in the effective-mass approximation. A defect having a deep character would have an electronic structure, and would exhibit a lattice distortion function of the chemical nature of the impurity and it will be hard to demonstrate that its electronic structure will be independent of the type of lattice site it occupies. To be convincing the calculations which are performed to justify the LLR model[42–44] should first show that the energy levels calculated are identical (within 30 meV) for all impurities whatever the site (As or Ga) they occupy.

Until recently it was widely admitted that the *DX* level was linked to the *L* band. However, when it has been realized that such property implies that the *DX* center must be an effective-mass state, the partisans of the LLR model started to question this statement, on the ground that the pressure derivative of the *DX* level is different from the one of the *L* band. In fact, great care must be used to derive a conclusion. First, this argument is not better than the one it pretends to destroy since the measurements of pressure derivatives of energy levels suffer the same difficulty, namely, a low accuracy, being performed using the same DLTS technique. Second, it is not clear if everybody agrees with the pressure derivative values of the bands and the conclusions which have been derived depend on the value taken for the pressure derivative of the Γ, L, and X bands.[45,46] Moreover the relative variations of the different bands versus x or pressure are not identical: for instance, the L and X bands do not cross each other for the same equivalent value of x versus pressure than versus x. More important is the fact that in regions where two bands have similar energies, mixing occurs and the DX level cannot be described anymore with L states only. This explains why the pressure derivatives change from a pure L character to a mixed one (between L and X) in the region where these bands are close in energy.

Very recently Shan *et al.*[47,48] reported a systematic study of the pressure derivative of the DX center which clearly demonstrates that it is equal to the L band one in the direct-band-gap material and to the X band one in indirect-band-gap material. These results can be easily understood with the DX level linked to the L band in both cases because this level becomes resonant above the X band in indirect-band-gap material. It is the X effective-mass state (located at 30–40 meV below the X band) which is detected in indirect material and which they attribute to the DX center, thus explaining why they observed an apparent variation of the ionization energy of the DX center when the pressure induces the transition direct to indirect band gap.

Actually, one should not expect that the change of the energy level is exactly equal to the band one, and the pressure derivative exactly equal, even for an effective-mass state which is deepened by a central-cell correction. The reason is that such a state, even built with the wave function ψ_L of one single band, could be sensitive to the central-cell potential. The pressure (or x) derivative of the energy level, in addition to the term $(\partial/\partial x)\langle \psi_L | H_0 | \psi_L \rangle$ corresponding to the Hamiltonian H_0 of the unperturbed crystal, which is the derivative of the band, contains also a term $(\partial/\partial x)\langle \psi_L | V | \psi_L \rangle$ due to the defect potential V. This second term is zero only in the case of a pure effective-mass state. Moreover, the local force constant of the impurity changes with electron trapping on the impurity site. This is equivalent to a lattice relaxation and should result in a change of the pressure derivative with the charge state.

The effective-mass model is in full agreement with the fact that the DX emission rate is sensitive to the Poole-Frenkel effect. Namely, it is a donor state characterized by a Coulomb potential, as expected for an effective-mass state. This last fact is very important because it rules out deep defects models. It rules out, in particular, the negative U models[42–44] which predict for the DX level a $0/-$ transition and not the $0/+$ transition necessary to account for the Poole-Frenkel effect. Indeed, within the LLR model, it is not conceivable that (i) two single donor levels, i.e., having the same electronic occupancy exist for the same impurity, and that (i) the defect potential is long range. As we mentioned briefly in Sec. I, the existence of E_C and of a large threshold for optical ionization can be qualitatively understood within the effective-mass model. However, there still remains questions to be answered, the main one being, if the optical ionization corresponds to a transition towards a state or a band higher in energy than the bottom of the conduction band, and not to the bottom of the conduction band, why is this last transition not observed? Could the low-energy transition be the one reported by Henning[49] and Lebedo,[50] whose existence is strongly denied by Mooney *et al.*?[15] According to Henning (see Ref. 16 in Ref. 49) a low-energy transition around 200 meV is indeed always observed but has been removed from the data of Mooney *et al.* because it does not exhibit any persistent effect. A threshold at this energy is indeed expected for the transition into the L band; this transition is also expected to be nonpersistent since the electron in the L band can recombine readily on the DX center.

V. STATISTICS OF OCCUPATION

The existence of two donor states in the gap, introduced by a single impurity, associated with, respectively, the Γ (or X) band and the L band, is an unusual situation. Usually, only one effective-mass state, of the lowest band, is located in the gap. Here the L associated state, because it is deepened by intervalley mixing, can also be located in the gap for specific alloy compositions. For this reason we have to examine the way the statistics of occupation is modified, as compared to the classical case.

For this we consider impurities in concentration N_D which give rise to two donor states, one shallow having a level located at E_S below the conduction band and another deeper one, located at E_{DX}. An impurity can be neutral or positively charged, when ionized; when the electron is located on one of its associated levels, E_S or E_{DX}, it is impossible to find another electron located on the other associated level, E_{DX} or E_S. When filled, these states have concentrations which are, respectively, N_S and N_{DX}. Since electrons in the band, in concentration n, are provided by the impurity, we have the following neutrality condition:

$$N_D = n + N_S + N_{DX} . \tag{2}$$

We proceed using the classical way to determine the most probable distribution of the electrons over the two levels. The number of distinct ways to distribute N_S electrons at the energy E_S over the N_D impurities is

$$W_S = \frac{N_D!}{N_S!(N_D - N_S)!} , \tag{3}$$

where (!) stands for the factorial function. The N_{DX} electrons, at the energy E_{DX}, are then distributed over the remaining $N_D - N_S$ impurities and the corresponding complexion number is

$$W_{DX} = \frac{(N_D - N_S)!}{N_{DX}!(N_D - N_S - N_{DX})!} . \tag{4}$$

Thus the total number of ways to distribute the $N_S + N_{DX}$ electrons over the N_D impurities is

$$W_T = W_S W_{DX} \tag{5}$$

that is

$$W_T = \frac{N_D!}{N_S! N_{DX}!(N_D - N_{DX} - N_S)!} . \tag{6}$$

With the origin of the energy at the bottom of the conduction band ($E_{\mathrm{CB}}=0$), the total energy of the system is

$$E_{T0}=N_S E_S+N_{DX}E_{DX} \ . \tag{7}$$

The most probable distribution is the one for which W_T is maximum, while E_{T0} and N_S+N_{DX} remain constant. It is obtained through the method of the Lagrangian multiplicators and using Stirling's formula to approximate the factorial function. The result is

$$N_D-N_S-N_{DX}=N_S\exp(\beta E_S-\mu) \ , \tag{8}$$

$$N_D-N_S-N_{DX}=N_{DX}\exp(\beta E_{DX}-\mu) \ , \tag{9}$$

with $\beta=(kT)^{-1}$ and $\mu=E_F/kT$ where E_F is the Fermi level.

From these two equations we get

$$N_S=N_D/[1+\exp(E_S-E_{DX})/kT+\exp(E_S-E_F)/kT] \tag{10}$$

and

$$N_{DX}=N_D/[1+\exp(E_S-E_{DX})/kT+\exp(E_{DX}-E_F)/kT] \tag{11}$$

The Fermi level

$$n=N_C\exp[-(E_{\mathrm{CB}}-E_F)/kT] \tag{12}$$

($E_{\mathrm{CB}}=0$), where N_C is the density of states in the conduction band, is obtained from the neutrality condition (2), and the result can be written in the classical form

$$E_F=E_C+kT\ln\chi \tag{13}$$

where χ stands for

$$\chi=\frac{-1+\{1+4(N_D/N_C)[\exp-(E_S-E_{\mathrm{CB}})/kT+\exp-(E_{DX}-E_{\mathrm{CB}})/kT]\}^{1/2}}{2[\exp-(E_S-E_{CB})/kT+\exp-(E_{DX}-E_{\mathrm{CB}})/kT]} \ . \tag{14}$$

In the case where E_S-E_{DX} is large compared to kT the expression of E_F reduces to

$$E_F\simeq E_{\mathrm{CB}}+\tfrac{1}{2}E_{DX}+kT\ln\left[\frac{N_D}{N_C}\right] \tag{15}$$

and the concentration of the filled *DX* center can be written

$$N_{DX}\simeq N_D/[1+\exp-(E_{DX}-E_F)/kT] \ . \tag{16}$$

Consequently, the way to deduce E_{DX} from the variation of the free-carrier concentration versus T^{-1} should be derived from

$$E_{DX}=2kT\ln[N_D(N_D-n)/N_C n] \tag{17}$$

that is, taking into account the temperature variation of N_C

$$E_{DX}=2k\frac{d[\ln T^{3/2}(N_D-n)/n]}{d(T^{-1})} \ . \tag{18}$$

This approximation should be valid below 100 K for x values ranging typically from 0.35 to 0.70.

VI. CONCLUSION

The fact that the *DX* energy level E_{DX} follows the L band is an indication that this defect is built with the state of the L band and, consequently, that this center must be the effective-mass state associated with this band. That the pressure derivative of E_{DX} is perhaps not equal to the pressure derivative of the L band and that it does not follow exactly the L band, should not be surprising since this effective-mass state is deepened, i.e., sensitive to the central-cell potential and the L band can be mixed with the other ones in specific ranges of the alloy composition.

These results do not constitute a proof for the L nature of the *DX* center, i.e., that it is the effective-mass state of the L band. This proof is found in the convergence of different types of observations. We have discussed some of them in the following:

(1) The independence of E_{DX} on the chemical nature of the impurity.

(2) The independence of E_{DX} on the site (As or Ga) of the impurity.

(3) The donor nature of the center, provided by the occurrence of the Poole-Frenkel effect when the DX level is close to the bottom of the conduction band.

(4) The existence of an associated long-range potential. There are other indications which we have discussed elsewhere.

(5) The variation of the capture barrier energy E_c versus x. It varies as $E_c(x)=B+\Delta(x)$ where B is a constant (~200 meV for Si and 0 meV for Te) and $\Delta(x)$ the energy difference between the L and the bottom (Γ or X) of the conduction band. Such variation means that an electron must be first excited from the bottom of the conduction band into the L band before it can recombine on the *DX* center, or equivalently that it is directly ionized from the *DX* level into the L band.[9] Once again, this variation cannot be accounted for by any of the LLR models.

(6) The existence or nonexistence of the *DX* center in superlattices in which the band structure is modified: the *DX* center is present when the L band is preserved and the other bands are modified in nature and energy position; it is absent when the L band is modified.[41,52]

In conclusion, all these observations find a natural explanation if the *DX* center is the effective-mass state of the L band deepened by intervalley mixing.

ACKNOWLEDGMENTS

Laboratoire de Physique des Solides is Unite associée au Centre National de la Recherche Scientifique.

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