PHYSICAL REVIEW B VOLUME 40, NUMBER 18 15 DECEMBER 1989-II

Metastable state of the *EL*2 defect in GaAs

H. J. von Bardeleben
Groupe de Physique des Solides de l'Ecole Normale Supérieure, Centre National de la Recherche Scientifique, Tour 23, 2 place Jussieu, 75251 Paris CEDEX 05, France

(Received 5 July 1989; revised manuscript received 18 September 1989)

We present an analysis of the pressure and alloy dependence of the *EL*2 ground and excited states. The results can be quantitatively interpreted if the *EL*2 metastable state is attributed to the $A_1(1s)$ effective-mass state associated with the L conduction-band minimum. The apparently contradictory results on the *EL*2 point symmetry obtained from optical absorption and optically detected electron-nuclear double-resonance studies find a simple explanation within this model.

The native donor defect *EL*2 belongs to one of the most studied defects in the III-V semiconductors.[1] Most of these studies have been performed in GaAs, but results on *EL*2 in the ternary III-V alloys have equally been reported.[2,3] In particular the metastability of *EL*2, which gives rise to a variety of associated phenomena such as persistent photoconductivity and acceptor neutralization, has incited numerous studies. In spite of this, the origin of this metastability as well as its correlation with a specific microscopic model is still the subject of controversy.[4–8] Currently, two different models for the metastable state implying larger lattice relaxations are actively discussed: The first one is the split interstitial As_i-As_i pair model[7] and the second a As_i-V_{Ga} model;[5,6] they are derived from two different ground-state configurations: As_{Ga}-As_i (Refs. 9 and 10) and As_{Ga} (Ref. 4). Based on very recent results on the hydrostatic-pressure dependence[11–13] of the *EL*2 defect properties, which complete previous ones for the alloy dependence in the Ga-As-P system,[2,14] we present here a different model for the metastable state of the *EL*2 defect. In the preceding modelings of the *EL*2 ground state and metastable state,[5–7] most of its main properties have been taken into account, however, with the following two notable exceptions: (i) the variation of the *EL*2 properties, when the defect is placed in a ternary alloy such as $GaAs_{1-x}P_x$ and (ii) their hydrostatic pressure dependence in the GaAs binary compound. Both perturbations, alloying and pressure, modify the conduction-band (CB) structure in a similar manner and lead to a modification of the metastability.[2,13,14] These results had not found any explanation up to now.

The point symmetry of *EL*2 in its stable configuration is equally still a matter of controversy: From optical absorption measurements under uniaxial stress[4] it has been deduced as T_D whereas optically detected electron-nuclear double resonance (ODENDOR) gives a lower C_{3V} symmetry.[10]

All these properties find a simple and quantitative interpretation in the model we propose here: It attributes the metastable *EL*2 state to the $A_1(1s)$ effective-mass state associated with the L CB minimum. In the metastable configuration one electron from the A_1 antibonding ground state has been transferred to the $A_1(1s)$ L CB state. The alloy and pressure dependence of the metastable state is that of the L CB minimum. At low temperatures the L CB states can persistently be populated in GaAs by optical excitation into the resonant T_2^{ab} antibonding state or by a direct transition to the $T_2(1s)$ L CB state, which we attribute in our model to the zero-phonon absorption line at 1.03 eV. The splitting of the zero-phonon line under uniaxial stress reflects the symmetry of the shallow donor states of the L CB minimum and not the local point symmetry of *EL*2 which is determined in the ODENDOR experiment. This model quantitatively relates for the first time the pressure and alloy dependence of the *EL*2 defect to that of the three CB minima Γ, L, and X. Speculations on the involvement of L CB related states in the *EL*2 metastability have been formulated before,[15,16] however, the experimental support was insufficient at that time.

The electronic structure of the As_{Ga} defect, the main or exclusive component of the *EL*2 defect, has been calculated by different authors.[17,18] Their results confirm the simple tight-binding picture[19] in which the As_{Ga} defect introduces a deep antibonding A_1^{ab} ground state in the gap and an excited antibonding T_2 state T_2^{ab} at ~1.0 eV. If the A_1^{ab} state is placed at the experimental determined position of $E_C-0.75$ eV (GaAs) the T_2^{ab} state is resonant with L CB (Fig. 1). As every deep defect, *EL*2 will give rise additionally to three series of hydrogenic excited states associated with CB minima Γ, L, and X.[20] Those related with Γ are very shallow with ionization energies of ≲5 meV, however, the lowest effective-mass states associated with L and X are expected to be deeper. In fact, by a

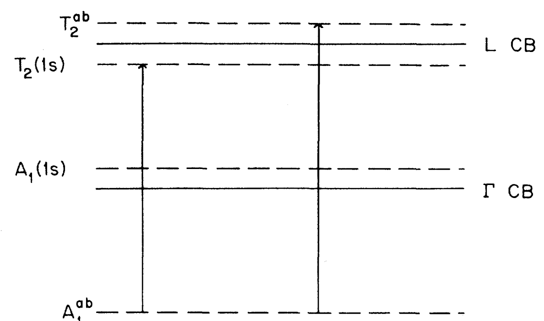

FIG. 1. Energy levels of the *EL*2 related ground and excited states.

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comparison with the $A_1(1s)$ state properties of double donor defects in the elemental semiconductors Si (Ref. 21) and Ge (Ref. 22) we expect the ground states to be deep with ionization energy of some 100 meV. Whereas direct optical transitions from A_1^{ab} to these shallow states have apparently not been reported up to now, transitions into the higher CB minima (L and X) have been observed before: The photoionization spectrum of the filled A_1^{ab} level to the CB shows three thresholds at 0.8, 1.1, and 1.3 eV, which have been attributed to the onsets of photoionization to the Γ, L, and X CB minima, respectively.[23] Due to the higher density of states of the L CB as compared to Γ, transitions to the L CB minimum are dominant for photon energies $E \gtrsim 1.1$ eV. Photoionization to the L CB occurs in the same energy range as the internal $A_1^{ab} \rightarrow T_2^{ab}$ transition centered at 1.2 eV.

Very recently the pressure coefficients for the zero-phonon absorption line at 1.03 eV and the intracenter absorption band at 1.2 eV have been determined.[11] The zero-phonon line shifts at a rate of 24.4 meV/GPa to higher energies whereas the intracenter transition shifts in the opposite sense at a rate of -26.4 meV/GPa. Both transitions have the same initial A_1^{ab} state but as demonstrated by the different pressure coefficients not the same final state. In order to relate their pressure coefficients to those of the CB minima, the shift of the A_1^{ab} state relative to the CB minima must be known. For an easier comparison we will express all pressure coefficients relative to the valence band in the following. First results have been obtained by White *et al.*[15] who have measured the pressure coefficients of the A_1^{ab} ground state with the double-source-differentiated-photocapacitance technique (DSDP) at pressure up to 8 K/bars; their results are $\partial E/\partial P = +12$ meV/GPa relative to the conduction band and $+17$ meV/GPa relative to the valence band as compared to a band-gap shift of 124 meV/GPa. However, Chantre, Vincent, and Bois[23] have shown that this method is unreliable in this case due to a mixing between the σ_n and σ_p spectra and we will therefore mainly consider the values determined by deep-level transient spectroscopy (DLTS) measurements. In a DLTS experiment the pressure coefficient of the electron emission rate is measured; its variation will depend on both that of the thermal ionization energy E_T and that of the thermal barrier E_C for electron capture. Thus a knowledge of the pressure dependence of the electron capture coefficient is necessary for the separation of the two terms. The pressure coefficient of the capture rate has been determined by Dreszer and Baj[12] to (-49 ± 5) meV/GPa. This value is close to the difference of the pressure coefficients of the Γ and L conduction bands. Zylbersztejn, Wallis, and Besson[24] determined the pressure derivative of the emission rate relative to the lowest Γ conduction band at 306 K as (38 ± 3) meV/GPa. Thus the A_1^{ab} state shifts with a coefficient $\partial E_T/\partial P = [38-(-49)]$ meV/GPa $=87$ meV/GPa relative to the Γ conduction band.

The pressure coefficients for the three conduction-band minima relative to the valence band have been determined by different authors (see Table I). Their results scatter by $\sim \pm 10$ meV/GPa; we will retain the following values: $\partial E(\Gamma)/\partial p = 115$ meV/GPa, $\partial E(L)/\partial p = 55$ meV/GPa, and $\partial E(X)/\partial p = -15$ meV/GPa.[25,26] From these values we deduce the value for the ionization to the lowest Γ CB: $(49+38)$ meV/GPa $=87$ meV/GPa. As Γ changes with 115 meV/GPa $\partial E_T/\partial P = (115-87)$ meV/GPa $=28$ meV/GPa, that is the A_1^{ab} ground state shifts with 28 meV/GPa relative to the highest valence band. The maximum uncertainty of this value, obtained by adding the individual errors for E_T, E_C, and Γ, is ± 18 meV/GPa.

TABLE I. Pressure coefficients relative to the valence band of the CB minima, zero-phonon line (ZPL), and intracenter transition (IT), electron emission energy and capture barrier as well as $EL2$ A_1^{ab} ground state relative to the Γ CB and highest VB.

	$\frac{\partial E}{\partial p}$ (meV/GPa)
CB minima	
Γ	115[a]
L	55[a]
X	-15[a]
ZPL	24.4[b]
IT	-26[b]
$\ln(E_T+E_C)$	38[c]
$\ln(E_C)$	-49[c]
$E(A_1^{ab})_\Gamma$	87
$E(A_1^{ab})_{VB}$	27

[a]References 25 and 26.
[b]Reference 11.
[c]References 12 and 24.

The value of 28 meV is close to the one deduced from photoluminescence measurements on the 0.68-eV band[27] and identical to the one predicted theoretically for the variation of an A_1 state of a defect on a Ga lattice site.[28] The pressure coefficient of a T_2 Ga state has also been evaluated by these authors; it is ~ 10 meV/GPa smaller than that of A_1 Ga,[28] which is in qualitative agreement with the variation of the absorption band at 1.2 eV ascribed to an intracenter transition.

We can now calculate the pressure derivative expected for an optical transition from the A_1^{ab} state to an effective-mass state of the L CB minimum: $(55-28)$ meV/GPa $=27$ meV/GPa. This value is close to the one determined for the zero-phonon line at 1.03 eV determined by Baj and Dreszer[11] as 24.4 meV/GPa from optical-absorption measurements at 4 K. Thus we attribute the zero-phonon line to the $A_1^{ab} \rightarrow T_2(1s)$ transition. An attribution of this line to a different final effective-mass state related to a different CB minimum, Γ or X, is excluded from both its energy of 1.03 eV as well as from the significantly different pressure derivatives of $(115-28)$ meV $=87$ meV/GPa and $(-15-28)$ meV/GPa $=-43$ meV/GPa, respectively.

Within this model the significance of the zero-phonon line splitting under uniaxial stress changes equally. It no longer reflects the point symmetry of the $EL2$ defect, but the symmetry of the L CB minimum. The splitting of the zero-phonon line under uniaxial stress along the [100], [111], and [110] directions up to stresses of 200 MPa has been measured by Kaminska, Skowronski, and Kuszko.[4]

These authors had attributed this line to the $A_1^{ab} \rightarrow T_2^{ab}$ transition. However, the very recently determined opposite pressure coefficients for the zero-phonon line and the intracenter transition at 1.2 eV, as well as their intensity ratio which is incompatible with the Huang Rhys factor of 6, exclude this attribution. The splittings of the $T_2(1s)$ donor state under uniaxial stress have been studied for the group-V donors in Ge, which has a lowest L CB minimum.[29] The $A_1^{ab} \rightarrow T_2(1s)$ transition is expected to split in 2, 3, and 2 components for stresses along [111], [110], and [100], respectively, in agreement with the experimental results obtained for $EL2$.[4] In this model the metastability of $EL2$ is not directly dependent on the presence of other defects associated with the As_{Ga} defect and thus the isolated As_{Ga} and the weakly interacting As_{Ga}-As_i pair models for the stable configuration of $EL2$ are compatible with these results. However, the new interpretation of the zero-phonon line splitting leaves the isolated As_{Ga} model without direct experimental support.

The application of hydrostatic pressure, which shifts the ground and effective-mass state of $EL2$, as well as the CB minima of $EL2$, also strongly modifies the metastability. For pressure $P \gtrsim 0.3$ GPa, Baj and Dreszer[13] observed that the $EL2$ ground state, which is persistently quenchable for $P < 0.3$ GPa can now be optically regenerated even at 4 K. The pressure-induced optical regeneration is observed both in n-type and semi-insulating material. This observation finds a simple explanation within our new model. The effect of the hydrostatic pressure is to move the $A_1(1s)$ L CB band-related state into the forbidden gap, which makes it optically and electrically active. The same process has been studied in detail for the single-donor defect DX in GaAs. In the case of the DX center, related to Si doping, pressures of 2 GPa are necessary for this crossover.[30] The fact that the same effect occurs for the $EL2$ related $A_1(1s)$ state at pressure as low as 0.3 GPa demonstrates that the $EL2$ related $A_1(L)$ level is deeper than the DX related shallow level and of the order of 290 meV (Fig. 2).

An additional confirmation for this model is obtained by the alloy dependence of the $EL2$ metastable state in the $GaAs_{1-x}P_x$ system, which has been studied by Samuelson and Omling in the 100-K temperature range.[2,14] Their results, which had not found an explanation at that time, are the following: in the $x = 0$ to $x = 0.30$ composition range the $EL2$ defect can be optically quenched into the metastable configuration. The optical-absorption band inducing this transformation changes neither the peak position nor the linewidth within this composition range. These results strongly favor that the absorption at 1.2 eV is due to an intracenter transition, which is apparently insensitive to alloy broadening effects. However, for $x > 0.3$ the $EL2$ defect is no longer metastable. Earlier studies of the nitrogen defect N_x, whose effective-mass states are mainly built from L and X CB states, have shown that at this composition $x = 0.30$ the shallow effective-mass state drops below the lowest Γ conduction band.[31] Within our model the metastability of the $EL2$ defect ceases for the same reasons: for $x > 0.3$ the $A_1(1s)$ L CB state drops below the Γ CB. Optical excitation can then lead to the formation of a negatively charged charge state of the metastable configuration. In this charge state the barrier for thermal regeneration is lowered to $T \approx 40$ K (Ref. 32) and no metastability is observable at 100 K.

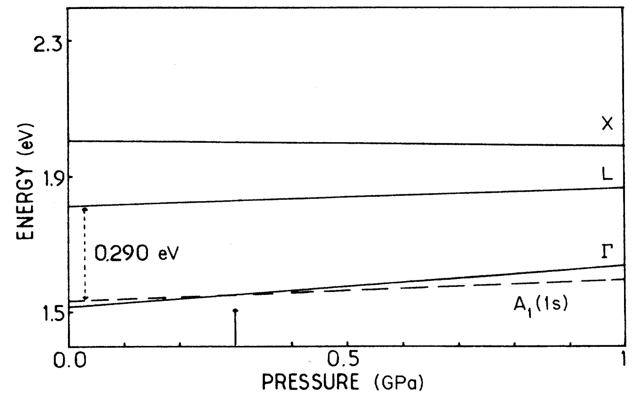

FIG. 2. Pressure dependence of the conduction band in GaAs.

We have shown in the preceding section that this new model gives a quantitative interpretation of the pressure dependence of the metastable $EL2$ state. However, we have not yet discussed why the electron in the $A_1(1s)$ state is metastable. The results presented here imply that the thermal emission of the electron from the $A_1(1s)$ L CB state can only proceed via the L conduction band in spite of the fact that this state is resonant with Γ CB. The activation energy for the regeneration of the stable state from the neutral metastable are thus $E_L - E_{A_1(s)} \approx 0.3$ eV. The metastability of this donor is very similar to the one observed for the simple donor DX in the $Ga_{1-x}Al_xAs$ alloy system. Low-temperature optical excitation with $E \gtrsim 0.8$ eV leads to the formation of an excited effective-mass state of the DX center, derived from the X CB minimum; in spite of being resonant with Γ this state is equally metastable.[33] No direct theoretical justification for this metastability has been proposed up to now except the involvement of a lattice relaxation effect.[34] Nevertheless, calculations of the combined influence of the impurity potential and the CB structure of GaAs on the lifetime of these resonant states are needed for an understanding of this phenomenon.

In conclusion, we have shown that the consideration of the pressure and alloy dependence of the $EL2$ metastability leads to a new model for the metastable state which is generated by the optically induced transfer of one electron from the A_1^{ab} ground state to the $A_1(1s)$ L CB minimum related effective-mass state. The metastability of resonant, effective-mass states derived from secondary CB minima should be of importance for other donors in GaAs and related III-V alloys.

I thank J. C. Bourgoin and M. Lannoo for many discussions. Groupe de Physique des Solides de l'Ecole Normale Supérieure is Laboratorie associé à l'Université Paris 7.

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