

## Donors in semiconductors and metastability

J. C. Bourgoin and 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*

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We observed that excited or ground effective-mass states of deep or shallow donor defects linked to the different conduction bands of the semiconductor can exhibit long lifetimes characteristics of their depth from the corresponding band. This way the metastable behaviors of the so-called *DX* center and *EL2* defects in GaAs and related alloys can be understood without the need to introduce distorted atomic configurations of these defects.

A substitutional impurity replacing an atom of the lattice gives rise to donor shallow effective-mass states associated with each of the conduction bands when the external shell of its electronic structure contains one more electron than the lattice atom it replaces. Thus, substitutional impurities of group-V in group-IV semiconductors and of group IV (on group-III lattice sites) in III-V compound semiconductors give rise to three effective-mass states associated with the  $\Gamma$ ,  $L$ , and  $X$  conduction bands. Only the effective-mass state associated with the lowest band lies in the forbidden gap and is populated at equilibrium. In the same way, a donor defect whose ground state lies deeper in the gap possesses a series of excited hydrogenic states associated with each band since they are bound by the Coulomb tail of the localized potential of the defect.

Often the excited or ground states associated with one particular band are not shallow as expected. This is, for instance, the case of the excited states of double donors in silicon. This is explained by introducing a so-called central cell correction (see, for instance, Ref. 1). The physical origin of this correction is often unspecified. For an  $L$  associated state it should be ascribed to a so-called shallow-deep instability induced by intervalley mixing.<sup>2</sup> Indeed, the  $L$  band contains several valleys (four in GaAs) and the treatment which account for their mixing in the Schrödinger equation of the effective mass is equivalent to the introduction of a central cell potential. This can also be the case for an  $X$  state since the  $X$  band contains three valleys.

Depending on the relative energy positions of the different conduction bands, the effective mass  $L$  (for instance) associated state will or will not lie in the forbidden gap. It is in the gap when the  $L$  band is the lowest one or when the difference  $\Delta$  between the  $L$  and the lowest ( $\Gamma$ ) bands is smaller than the ionization energy  $E_L$  of this  $L$  state. The aim of this Rapid Communication is to show that when one of the effective-mass states is relatively deep relative to its own band but still located above the bottom of the conduction band because the corresponding band is not the lowest one, an apparent metastability phenomenon is observed. We shall see that the metastable properties associated with the so-called native *EL2* deep defect in GaAs and with the *DX* center related to the substitutional donor impurity in GaAs alloys find this way a simple explanation which do not require the introduction

of metastable, distorted, atomic configurations.

For this we consider a system such as GaAs for instance, containing three conduction bands;  $\Gamma$ ,  $L$ ,  $X$ . The ionization energies of the associated effective-mass states of a substitutional impurity relative to their corresponding bands are noted respectively  $E_\Gamma$ ,  $E_L$ , and  $E_X$ . We assume  $E_L$  to be deep due to the mixing between the four  $L$  valleys, an assumption which has been quantitatively justified.<sup>2</sup> Two cases have to be considered: (a)  $E_L$  is smaller than the energy difference  $\Delta(L - \Gamma)$  between the  $L$  and  $\Gamma$  bands so that the  $L$  associated state lies above the bottom of the  $\Gamma$  conduction band; (b)  $E_L$  is larger than  $\Delta(L - \Gamma)$ , when  $\Delta(L - \Gamma)$  is reduced by alloying, or hydrostatic pressure.

In case (b),  $E_L$  being deeper than  $E_\Gamma$ , the electrons provided by the donor impurity occupy the  $E_L$  level. When they are optically or thermally excited they relax to the bottom of the conduction band ( $\Gamma$ ). Then, in order to recombine on the  $E_L$  level, they must be first excited into the  $L$  band. Thus the recombination is characterized by a barrier  $\Delta(L - \Gamma)$ . Since this barrier can be large compared to  $E_\Gamma$  and of the order of  $E_L$  (depending on the alloy composition or pressure), electrons remain in the conduction band as long as their thermal ionization over this barrier cannot take place: It is the so-called persistent photoconductivity effect.

In case (a), the  $L$  level is resonant. In principle the characteristic time  $\tau$  of occupancy of such a level is  $\hbar W^{-1}$  where  $W$  is the width of the level. A typical value of  $W$  for an effective-mass state, as calculated,<sup>3</sup> is 10 meV which gives  $\tau \sim 10^{-15}$  s. However, experimentally we find this time  $\tau$  to be considerably larger. In Sn-doped GaAlAs where the Al composition is 0.31 (i.e., a material in which the  $X$  band is above the  $\Gamma$  and  $L$  ones) we observed,<sup>4</sup> by electron paramagnetic resonance after photoexcitation above 0.8 eV, the filling of the  $X$  associated state. The decay of the signal after the excitation is stopped is characterized by a long-time constant at 4 K (see Fig. 1). This time constant varies with the temperature indicating an associated activation energy of few meV. This result therefore strongly suggests that the  $X$ -associated level becomes empty when the electron is emitted thermally into the  $X$  band, i.e., that it does not interact directly with the states of the other bands but indirectly through the  $X$ -band states. Similarly the  $L$ -associated lev-

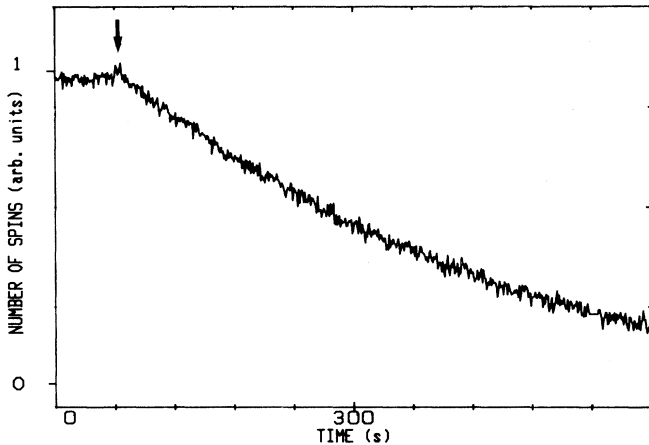


FIG. 1. Variation vs time of the number of spins detected after the photoexcitation is stopped (indicated by the arrow) at 4.2 K.

el remains occupied as long as the temperature is low enough to prevent the thermal ionization over the energy  $E_L$ ; the  $L$  level behaves apparently as a metastable state since  $E_L$  is relatively large. This is demonstrated by two experiments. First, the use of hydrostatic pressure in GaAs permits the filling of the  $L$  associated state  $E_L$  by its introduction in the gap. Once the pressure is removed the electron remains in this state<sup>5,6</sup> up to 110 K the temperature at which the ionization process occurs. Second, the capture barrier varies with the alloy composition as  $\Delta(L-\Gamma)$  in direct gap and  $\Delta(L-X)$  in indirect gap materials (see Fig. 2 for Te-doped materials; similar results for Si doped materials are given in Refs. 7 and 8).

It therefore appears that electrons bound on resonant effective-mass states must first be excited into their corresponding band before they can relax to the bottom of the conduction band, when the different conduction bands are independent. Longer electron lifetimes occur for deeper effective-mass states, as expected theoretically.<sup>9</sup>

The  $L$  effective-mass state in GaAs and GaAs alloys is the so-called  $DX$  center. This defect, whose concentration is practically equal to the donor doping concentration,<sup>10</sup> is located around 200 meV below the  $L$  band, whatever the nature of the impurity and the lattice site it occupies.<sup>7</sup> That this level is, as the shallow  $\Gamma$  effective-mass state, also a single-donor state is provided by the fact that it is sensitive to the Poole-Frenkel effect (which can only be detected<sup>11</sup> only in specific conditions). This defect has often been ascribed to a distorted configuration of the substitutional donor impurity (such as a negative  $U$  center<sup>12</sup>), based on the observation<sup>8,13</sup> that the thermal ionization energy (0.4 eV for Si) is smaller than the apparent optical ionization energy (0.8 eV). However, such so-called "large lattice relaxation" (LLR) model is in contradiction with the fact that this photoionization populates the  $X$  associated state in direct band material<sup>4</sup> as we have discussed above. Indeed, this implies that the assumption made to justify the LLR model, namely that the photoionization process observed correspond to the ionization from

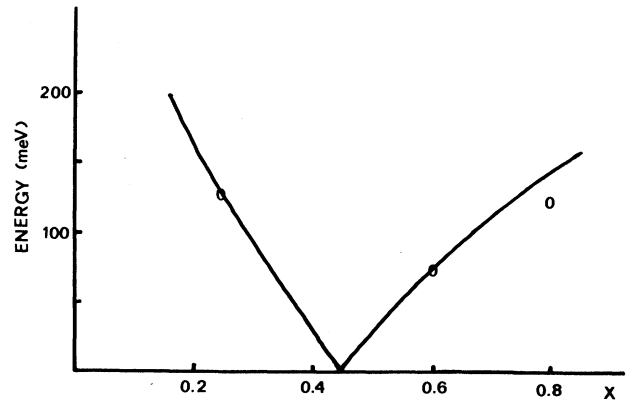


FIG. 2. Variation of the electron-capture barrier height of the  $DX$  level vs alloy composition  $X$  in Te-doped materials. The solid line sketches the energy difference between the  $L$  band and the bottom ( $\Gamma$  or  $X$ ) of the conduction band.

the  $DX$  level to the bottom of the conduction band, is invalid. (In fact, an optical threshold around 0.2 eV is also observed<sup>14,15</sup> which according to Ref. 14 was removed from the data in Refs. 13 and 16.)

In GaAs and alloys there also exist a deep donor level, associated with a native defect labeled  $EL2$  which is known to be directly related with the As antisite, a double donor (for a review on the  $EL2$  defect see Ref. 17). Photoexcitation at 0.8 eV induces the population of a metastable state which cannot be detected whatever the technique used. It is an excited state of the system because the charge state of the defect is not changed.<sup>18</sup> Several attempts have been made to explain the existence of this metastable state by introducing a new atomic configuration for the defect.<sup>19-21</sup> However, once again this metastability find a simple explanation if the excited state is nothing but the effective  $L$  associated state deepened by interval mixing. Evidences for the fact that this excited state is linked to the  $L$  band are not described here because they are given in Ref. 22. This metastability disappears, as in the case of the  $DX$  center, when this  $L$  excited state is made to emerge in the gap<sup>23</sup> using variable alloy composition. Note that, although this metastability can be understood for the simple As antisite, there are other observations (see Ref. 17) which strongly indicate that the  $EL2$  defect is a complex involving  $As_{Ga}$  and a As interstitial.

In conclusion, deep or shallow donor defects can induce metastability effects especially when the associated effective-mass states undergo a shallow-deep instability. The metastability of an electron localized on a resonant effective-mass state is directly related to its ionization into the corresponding band. There is thus no need to invoke the existence of a metastable atomic configuration to explain this phenomenon.

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