Metastable State of *EL*2 in GaAs

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The metastable state of the *EL*2 defect in GaAs is characterized by the absence of any experimentally observed defect level. We present a model of its atomic configuration, which allows a simple interpretation of this nonobservation as well as the direct and reverse transitions from the stable to this metastable state. The model consists of a split interstitial configuration of the initial stable $\mathrm{As_{Ga}}$-As_i pair. We first use simple physical arguments to show that this configuration has the required electronic properties. We then substantiate these arguments by a full calculation of the local atomic configuration and of the corresponding electronic structure.

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The *EL*2 defect in GaAs can exist at low temperature in two different atomic configurations.[1] The first one, corresponding to the stable state (usually called 0) is well characterized and has been recently attributed to an arsenic antisite ($\mathrm{As_{Ga}}$)–arsenic interstitial (As_i) pair at a second-nearest-neighbor distance.[2-4] On the other hand, the metastable state (0^*) is characterized by the absence of any direct experimental observation. In particular, it does not give rise to any paramagnetic defect state; no electrically active state has been detected by deep-level transient spectroscopy in the temperature range (below 140 K) in which it exists and it does not give rise to any optical absorption in the near-infrared region. There is thus no detailed information on the state 0^* known to be induced by photoexcitation.[1,5] The aim of this Letter is to propose and *justify* an atomic model for this metastable 0^* state. We shall see that its atomic configuration can be viewed as a split interstitial in which the two central As atoms (corresponding to the antisite and the interstitial of the 0 state) become trivalently bonded as in elemental crystalline and amorphous As.

One of the characteristic features of the *EL*2 defect[1] is that the $0 \rightarrow 0^*$ transition occurs at low temperature under 1.1-μm photoexcitation. The defect then remains in the 0^* configuration until the temperature is increased above 140 K in semi-insulating material. The whole transformation is achieved without change in charge state which means that the 0^* configuration is metastable.[5] From the absence of any paramagnetic spectrum associated with $\mathrm{As_{Ga}}$ in the 0^* configuration[3,6] one gets strong evidence that the $0 \rightarrow 0^*$ transition corresponds to the jump of As_i located in second-neighbor position of $\mathrm{As_{Ga}}$ to a closer interstitial position. This would not be the case if 0^* were a more distant pair since $\mathrm{As_{Ga}}$ in the pair would then behave in a way similar to the isolated antisite, the paramagnetic properties of which are known. The most straightforward hypothesis (as 0 corresponds to the pair at a second-nearest-neighbor distance) is then to consider that 0^* corresponds to As_i at a nearest-neighbor's position.[3] This possibility was analyzed theoretically in detail by Baraff and Schlüter[7] who, however, did not include the effect of possible lattice reorganization around the pair. It is such an effect that we want to consider here.

The present model is based on the fact that the coordination of elemental arsenic in the crystalline and amorphous form is trivalent. It thus seems natural that the close defect pair $\mathrm{As_{Ga}}$-As_i will take the split-interstitial form schematically pictured in Fig. 1(a).[8] This allows the two central arsenic atoms to be in their normal trivalent situation. However, the four nearest neighbors of Fig. 1(a) cannot stay at their perfect lattice positions since this would result in highly compressed interatomic distances within the cube. There must then be substantial lattice relaxation around this defect to release most of the associated elastic energy. This leads to the final asymmetric configuration of Fig. 1(b) as will be discussed later.

At this point it is interesting to get a rough idea of what could possibly be the electronic structure of such a split-interstitial configuration. For this we use a tight-binding molecular description similar to what can be done in GaAs and As. Within the cube of Fig. 1(a) one builds molecular states from the following atomic orbitals: (i) the four sp^3 hybrids pointing from the four nearest neighbors towards the two central arsenic atoms,

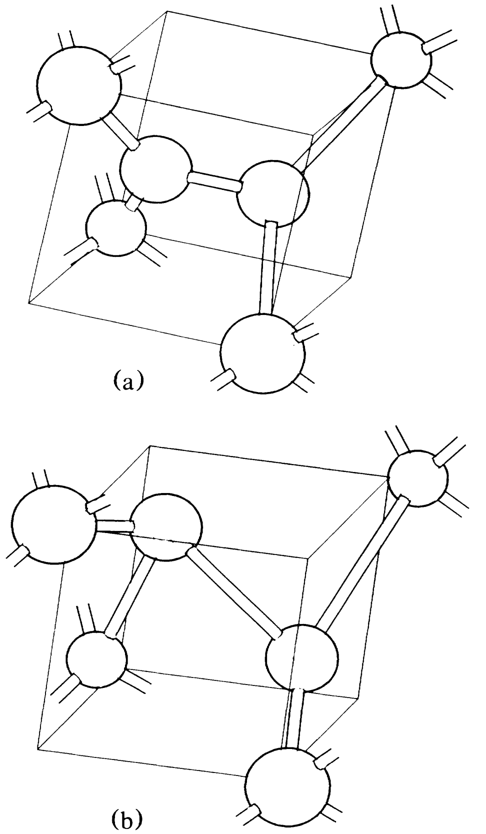

FIG. 1. Local atomic structure of the split interstitial (a) with no lattice relaxation and (b) the calculated asymmetric situation. In this case the coordinates of the two central atoms are ($\pm 0.89, 0.69, \mp 0.70$) Å while the displacement coordinates of A and C are ($\pm 0.30, 0.11, \mp 0.018$) Å and those of B and D are ($\pm 0.15, \mp 0.064, \mp 0.037$) Å.

(ii) three p orbitals on each As atom of the pair pointing approximately towards the neighbors, (iii) one s orbital on each As atom of the pair. In view of the large value ($\simeq 10$ eV) of the difference between s and p atomic energies one can treat the s states as essentially decoupled from the other states. All other states will then interact by pairs to form bonding σ and antibonding σ^* states (there will be four sp^3-p bonds and one p-p bond). These bonds will be strongly covalent so that we expect the σ-σ^* splitting to be larger than the GaAs gap, leading to the situation depicted in Fig. 2(a), characterized by the absence of gap states. This means that the charge state of the defect is determined since there are two electrons per bonding state and two per s state, i.e., a total of fourteen electrons. As a neutral complex would contain fifteen electrons (five on the sp^3 orbitals of the Ga vacancy and five per As atoms of the pair) the split-interstitial configuration as just described can only correspond to a + charge state.

If these simple arguments are valid, the split-interstitial defect fulfills two essential requirements: (i) It yields no gap levels, in agreement with existing experimental data, (ii) it only exists in the + charge state which precisely corresponds to the quenchable charge state of the 0 configuration,[9,10] in agreement with the fact that the charge state does not change in the $0 \rightarrow 0^*$ transformation. Of course a definitive test of the validity of our proposal must be experimental. As this is not yet the case, we have performed fairly detailed calculations in order to give strong support to the previous arguments. We have proceeded in two steps: (i) a determination of the minimum-energy configuration to find the local atomic structure and (ii) an electronic structure calculation for this configuration to determine the change in density of states.

At present it is impossible to perform a first-principles total-energy calculation for such a complex defect as the split-interstitial pair. To get an idea of the possible atomic configuration, we thus proceed in a different way. We use a valence force-field model where the elastic energy takes the form

$$E_{\mathrm{el}} = \tfrac{1}{2}\textstyle\sum_B k_{rB}(\Delta r_B)^2 + \tfrac{1}{2}\sum_\alpha k_{\theta,\alpha}(\Delta\theta_\alpha)_2 , \qquad (1)$$

where Δr_B is the change in bond length of bond B while $\Delta\theta_\alpha$ is the change in bond angle between two adjacent bonds. (This change is evaluated with respect to the normal tetrahedral angle 109° for tetravalent atoms and the normal angle 97° for trivalent As.) Such an expression is certainly valid as long as the atomic configuration corresponds to well-defined covalent bonds which is precisely the implicit assumption contained in the split-interstitial model. We thus apply expression (1) considering that all atoms are tetravalently bonded except for the two central atoms in Fig. 1(a) which make trivalent bonds. We then minimize expression (1) numerically for all six atoms of Fig. 1(a). This corresponds to a system of equations with eighteen unknowns. We include the influence of the surrounding crystal by attaching effective force constants to the four outer As atoms of Fig. 1(a). These are calculated from Green's-function theory as was done by Lannoo and Allan[11] for silicium (details about the whole procedure will be given in a separate publication).[12] The absolute minimum configuration is pictured in Fig. 1(b) which corresponds to a highly asymmetric situation for reasons discussed in detail in Ref. 12. The force constants are those deduced from bulk GaAs and As, but the atomic positions are found to be relatively insensitive to changes in these values.

The following step is then to perform an electronic structure calculation for the atomic configuration of Fig. 1(b). This is done in a tight-binding Green's-function approach including interactions up to second nearest neighbors as described by Talwar and Ting.[13] The other interactions involve the central atoms 1 and 2. Each of them has three nearest neighbors ($d_{12} = 2.27$ Å,

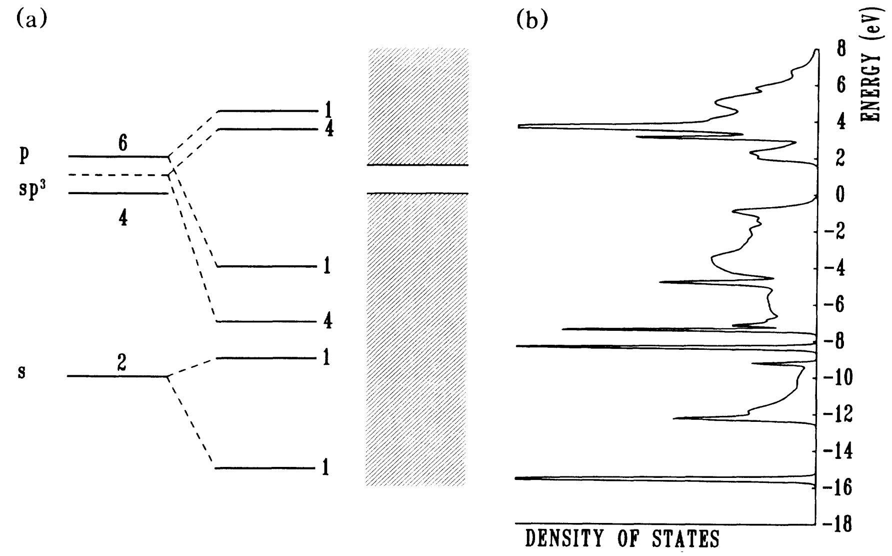

FIG. 2. (a) Schematic level scheme in the molecular model of the split interstitial with respect to the band gap (the numbers indicate the degeneracy of the levels). (b) Local density of states on one of the two central As atoms in the configuration of Fig. 1(b).

$d_{1A}=d_{1B}=d_{2C}=d_{2D}=2.38$ Å) and the corresponding interatomic terms are deduced from Harrison's rules.[14] We also include the influence of close second-nearest neighbors at distances like $d_{2D}=2.8$ Å for which we consider the interactions to be reduced by a factor of 2 with respect to nearest neighbors (the reasons for this are given in Ref. 12). Approximate self-consistency is realized by our shifting the atomic levels in such a way that local neutrality is achieved (this method is discussed by Priester, Allan, and Lanoo[15]). To summarize the results, we give in Fig. 2(b) the local density of states on one of the two central As atoms. No gap levels are obtained and the strong peaks can be directly assigned to *s*, bonding, and antibonding states as in the simple molecular model. The full calculation thus confirms the simple qualitative picture presented above.

Thus according to Ref. 9 and the above discussion, our present understanding of the $0 \leftrightarrows 0^*$ transformation is the following: The state 0 is the second-nearest-neighbor $\mathrm{As_{Ga}}$-As_i pair and 0^* the split-interstitial pair. The paramagnetic state of 0 is 0^{++}, corresponding to $\mathrm{As_{Ga}^{+}}$-As_i^{+}; its quenchable state 0^+ is $\mathrm{As_{Ga}^{0}}$-As_i^{+}. The optical excitation at 1.1 eV inducing the $0 \rightarrow 0^*$ transformation corresponds to an internal transition as confirmed by recent theoretical work.[16] As we have seen, the charge state in the split-interstitial configuration is $(0^*)^+$, i.e., the $0 \rightarrow 0^*$ transformation occurs at constant charge state as is observed experimentally. The thermal regeneration from $(0^*)^+$ to 0^+ occurs above a potential barrier of 0.3 eV.[17] Finally, the $(0^*)^+$ can bind an electron in a shallow donor state which, as discussed in Ref. 9, can explain the enhancement of the regeneration by the so-called Auger process[17] through the trapping of such an electron followed by the relaxation to the normal configuration.

In conclusion, we have proposed and justified theoretically an atomic model of the metastable configuration of *EL*2 in GaAs. This model, based upon the general tendency of As to form trivalent bonds, explains simply the absence of any experimental detection. Of course, a full confirmation of its validity will require direct experimental observation. Laboratoire de Physique des Solides is a Laboratoire Associé au Centre National de la Recherche Scientifique. Groupe de Physique des Solides de l'Ecole Normale Supérieure is a Laboratoire Associé à l'Université de Paris VII.

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