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# Atomic configuration and electronic properties of the metastable state of the *EL*2 center in GaAs

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A detailed study of the atomic and electronic structure of a recently proposed model for the metastable state of the *EL*2 center in GaAs is presented. This consists of a split $\mathrm{As}_i$ interstitial configuration. The important lattice reorganization around the split $\mathrm{As}_i$ pair is calculated in a new renormalized valence-force-field model. This leads to a somewhat asymmetric situation for the $\mathrm{As}_i$ pair. Secondly, the electronic properties of such a split $\mathrm{As}_i$ interstitial configuration are investigated through a Green's-function calculation. Both results are justified by simple qualitative arguments. The main conclusion is that the metastable split interstitial form exists only in the + charge state. This is the same charge state as that recently proposed as well for the stable state of the pair.

## I. INTRODUCTION

The *EL*2 center is a native, metastable defect in GaAs which has been intensively studied due to its important electronic properties.[1] Although several points are still unclear, important progress has been made recently in the understanding of this defect.[1] The *EL*2 center can exist in two different states. The first one is the normal or stable state for which von Bardeleben *et al.*[2–4] have proposed a model consisting of an arsenic antisite $\mathrm{As}_{\mathrm{Ga}}$ with an arsenic interstitial $\mathrm{As}_i$ nearby. Although this identification is not yet unanimously accepted, this model is now supported by several theoretical and experimental studies.[5–8] The *EL*2 center in the stable state gives rise to levels in the gap[5,9] and has an electron paramagnetic resonance (EPR) spectrum very close to that of the isolated $\mathrm{As}_{\mathrm{Ga}}$ antisite.[9] The fact that the interstitial $\mathrm{As}_i$ is not observed in the pair—and also the isolated interstitial—in contradiction with theoretical calculations,[10] has been explained recently by Lannoo[11] in terms of a large Jahn-Teller effect. This was then confirmed by a much more detailed calculation by Baraff, Lannoo, and Schlüter for $\mathrm{As}_{\mathrm{Ga}}$-$\mathrm{As}_i$ pair.[12]

The metastable state, being induced by optical absorption,[1,13] seems to be characterized by the absence of any experimentally observed defect level. The transition from the stable to the metastable state is made without change in charge state.[6,8] A mechanism for the metastability has been advanced[14,15] where the interstitial moves closer to the antisite so that the electronic properties of the antisite are completely modified. However, there is yet no information concerning the atomic configuration of this state. Our aim in this paper is thus to propose a model for the atomic structure of the metastable state of the *EL*2 center.[16] We show that the two As of the pair tend to become trivalent as in amorphous elemental As. For this, we calculate the atomic configuration of the pair using a valence-force-field model. As the entire calculation is a very hard task, we introduce a new renormalized valence-force-field model which allows to take into account only a small cluster composed by the two As and their four neighbors. Using this atomic configuration, we then show using a Green's-function calculation that the electronic structure of the pair is compatible with the experimental evidence. We finally discuss and justify our results by using simple physical models both for the atomic configuration and the electronic structure.

## II. MODEL FOR THE ELASTIC ENERGY OF THE *EL*2 CENTER IN THE METASTABLE STATE

As the stable state of the *EL*2 center (usually called 0) probably corresponds to an $\mathrm{As}_{\mathrm{Ga}}$-$\mathrm{As}_i$ pair,[2–5] it is reasonable to suppose that the metastable state ($0^*$) corresponds to the same interstitial $\mathrm{As}_i$ either closer to or more distant from the antisite $\mathrm{As}_{\mathrm{Ga}}$. The distant pair should have the same behavior as the isolated antisite and therefore would be EPR active.[4,14] As this is not the case, the transition $0 \Longrightarrow 0^*$ is probably connected to a motion of the $\mathrm{As}_i$ towards the $\mathrm{As}_{\mathrm{Ga}}$. Baraff and Schlüter[17] have analyzed the first-neighbor distance pair which is the simplest situation. They found that in this case an electrical level should be observed in the gap in contradiction with the experiment. Nevertheless, a lattice reorganization is possible, and then, another atomic configuration might be expected.

To have an idea of this new configuration, we view the metastable state of the *EL*2 defect as an inclusion of six As atoms ($\mathrm{As}_i$, $\mathrm{As}_{\mathrm{Ga}}$, and their four As neighbors) in a void surrounded by Ga atoms. Elemental arsenic is trivalent and it thus seems natural that the two extra As ($\mathrm{As}_{\mathrm{Ga}}$ and $\mathrm{As}_i$) tend to become trivalent, i.e., tend to be in an electronic configuration similar to the one occuring in amorphous arsenic. This leads to the split-interstitial form depicted in Fig. 1(a). Obviously, an important elastic energy should be associated with this kind of structure if the four nearest neighbors of Fig. 1(a) stay at their perfect lattice position. Therefore, we are going to analyze the relaxation induced in such a system to get an idea of the cost in elastic energy and of the atomic configuration in the metastable state.

As a full first-principles total energy minimization of such a defect pair is practically impossible at present, we proceed in a different way and write the elastic energy $E_{\mathrm{el}}$ under a valence-force-field form:

$$E_{\mathrm{el}}=\tfrac{1}{2}\sum_{B} k_{r,B}(\Delta r_B)^2+\tfrac{1}{2}\sum_{\alpha} k_{\theta,\alpha}(r_B\Delta\theta_\alpha)^2 , \tag{1}$$

where $\Delta r_B$ is the change in bond length $r_B$ of the bond $B$ while $\Delta\theta_\alpha$ is the change in bond angle between the two adjacent bonds. Such an expression is certainly valid provided that the atomic configuration corresponds to well-defined covalent bonds which is precisely implicit in our model. Making the assumption that the two central As atoms tend to become trivalent, we consider only bonds schematized by lines in Fig. 1. There are five bonds in this system: two for each of the two central As (namely, atoms 1 and 2 in the figure) with its two neighbors and one between them. The changes in the bond angles $\Delta\theta_\alpha$ are evaluated with respect to the normal tetrahedral angle 109° for tetravalent atoms (i.e., the four neighbors). For the two As (1 and 2), this change is referred to the normal angle 97° for trivalent As (amorphous As). The change in bond length is calculated with respect to the amorphous As bond length which is close to the interatomic distance in GaAs.

Even the calculation of the elastic energy of the defect under this simple form is a very hard task: indeed, the relaxation of the pair and its surroundings induces deformations in the whole crystal. Even if these deformations are small far from the defect, it is impossible to neglect long-range effects. Two common approaches to such a problem are the use of a large cluster calculation[18] or a Green's-function technique.[19] We shall develop here a model which considerably reduces the complexity of the calculation. We will see that it is possible using effective force constants to consider only a small cluster composed by the pair and its four neighbors. This approach is built in the same spirit as the concept of renormalization developed for transition metal ions in semiconductors.[20]

## III. ENERGY MINIMIZATION WITH RENORMALIZED FORCE CONSTANTS

We first show here how it is possible to introduce formally the concept of effective or renormalized force constants. For this let us write the elastic energy of the defect explicitly in terms of the positions $\mathbf{R}_\alpha$ $(\alpha=1,2)$ of the two central atoms of Fig. 1 and also of the displacements $\mathbf{u}_i$ of all other bulk atoms with respect to their perfect lattice position. This gives

$$E=E(\mathbf{R}_\alpha,\mathbf{u}_i)=E_0(\mathbf{u}_i)+\delta E(\mathbf{R}_\alpha,\mathbf{u}_i) , \tag{2}$$

where $E_0(\mathbf{u}_i)$ is the elastic energy of a perfect crystal with a central Ga vacancy and $\delta E(\mathbf{R}_\alpha,\mathbf{u}_i)$ is the additional energy due to the introduction of the two extra As atoms. It is important to note that the additive term $\delta E$ is of short-range character and that consequently only a few $\mathbf{u}_i$ must be included in the mathematical expression of $\delta E$. In the following, we will consider that the $\mathbf{u}_i$ are components of a column matrix $\underline{u}$ in which one part $\underline{u}_0$ occurs in $\delta E$ and the remaining part $\underline{u}_R$ does not. Then

$$\delta E(\mathbf{R}_\alpha,\mathbf{u}_i)=\delta E(\mathbf{R}_\alpha,\underline{u}_0) . \tag{3}$$

The elastic energy $E_0$ can be expanded to second order in the atomic diplacements. This gives

$$E_0=\tfrac{1}{2}\underline{u}^{\dagger}\underline{A}\,\underline{u} , \tag{4}$$

where $\underline{A}$ is the force-constant matrix. It is then easy to minimize $E$ with respect to $\underline{u}_R$. This leads to

$$(\underline{A}\,\underline{u})_R=\underline{0} . \tag{5}$$

The matrix $\underline{A}$ can be written in four blocks using the same basis as for $\underline{u}$:

$$\underline{A}=\begin{bmatrix}\underline{A}_{00} & \underline{A}_{0R}\\ \underline{A}_{R0} & \underline{A}_{RR}\end{bmatrix} . \tag{6}$$

The relation (5) can be rewritten as

$$\underline{A}_{RR}\underline{u}_R+\underline{A}_{R0}\underline{u}_0=\underline{0} \tag{7}$$

and, using (2), (4), and (6), we can expand the energy $E$:

$$\begin{aligned}E(\mathbf{R}_\alpha,\underline{u})=\delta E(\mathbf{R}_\alpha,\underline{u}_0)&\\ +\tfrac{1}{2}(\underline{u}_0^{\dagger}\underline{A}_{00}\underline{u}_0+\underline{u}_0^{\dagger}\underline{A}_{0R}\underline{u}_R&\\ +\underline{u}_R^{\dagger}\underline{A}_{R0}\underline{u}_0+\underline{u}_R^{\dagger}\underline{A}_{RR}\underline{u}_R)&\end{aligned} \tag{8}$$

which can be simplified using relation (7) as

$$\begin{aligned}E(\mathbf{R}_\alpha,\underline{u})=\delta E(\mathbf{R}_\alpha,\underline{u}_0)&\\ +\tfrac{1}{2}(\underline{u}_0^{\dagger}\underline{A}_{00}\underline{u}_0-\underline{u}_0^{\dagger}\underline{A}_{0R}\underline{A}_{RR}^{-1}\underline{A}_{R0}\underline{u}_0) .&\end{aligned} \tag{9}$$

Equation (9) still looks rather complicated since there are terms which depend on $R$ (i.e., characteristic of the whole crystal). Nevertheless, it can be transformed using Green's-function theory.

We introduce the matrix of the resolvent operator $\underline{G}$ defined by Refs. 19 and 21 ($\underline{I}$ being the identity matrix)

$$\underline{G}=\lim_{\epsilon\to 0^+}[(\omega^2+i\epsilon)\underline{I}-\underline{A}]^{-1} . \tag{10}$$

We can split the matrix $\underline{G}$ in the same manner as $\underline{A}$ in (6). It is also interesting to consider the Green's function $g$ associated with the matrix $\underline{a}$ defined by

$$\underline{a}=\begin{bmatrix}\underline{A}_{00} & 0\\ 0 & \underline{A}_{RR}\end{bmatrix} . \tag{11}$$

In this case, the elements depending on $\underline{u}_R$ and $\underline{u}_0$ are decoupled. The Dyson equation gives a relation between the matrices $\underline{G}$ and $\underline{g}$

$$\underline{G}=\underline{g}+\underline{g}\underline{V}\,\underline{G} , \tag{12}$$

where the coupling matrix $\underline{V}$ is simply given by

$$\underline{V}=\begin{bmatrix}0 & \underline{A}_{0R}\\ \underline{A}_{R0} & 0\end{bmatrix} . \tag{13}$$

The application of Dyson's equation allows one to write

$$\underline{G}_{00}=\underline{g}_{00}+\underline{g}_{00}\underline{A}_{0R}\underline{G}_{R0} ,$$

and (14)

$$\underline{G}_{R0}=\underline{g}_{RR}\underline{A}_{R0}\underline{G}_{00} .$$

From (14), we deduce

$$\underline{G}_{00}^{-1}=\underline{g}_{00}^{-1}-\underline{A}_{0R}\underline{g}_{RR}\underline{A}_{R0} . \tag{15}$$

This relation (15) can be applied to the particular case where $\omega=0$ [then we have $\underline{G}(\omega=0)=-\underline{A}^{-1}$]. This gives

$$\underline{G}_{00}^{-1}(\omega=0)=-(\underline{A}_{00}-\underline{A}_{0R}\underline{A}_{RR}^{-1}\underline{A}_{R0}) . \tag{16}$$

Using (16), we obtain a formally simpler expression for the elastic energy $E_0^*$ (obtained by minimizing $E_0$ with respect to $\underline{u}_R$):

$$E_0^*(\underline{u}_0)=\tfrac{1}{2}\underline{u}_0^{\dagger}[-\underline{G}_{00}^{-1}(\omega=0)]\underline{u}_0 . \tag{17}$$

Lannoo and Allan[19] have shown that the matrix $[-\underline{G}_{00}^{-1}(\omega=0)]$ corresponds to effective or renormalized force constants. Therefore the signification of Eq. (17) is simple: the calculation of the elastic energy of the whole system can be reduced to that of a small cluster, provided that the influence of the remainder of the crystal is taken into account through the use of effective force constants. The cluster size is given by the range of the force induced by the defect. In our particular case, we only consider the two central As atoms and the four neighbors of the pair. The cluster studied is represented in Fig. 1(a), the four neighbors of the As pair being $A$, $B$, $C$, and $D$. Due to the local symmetry, these atoms can be treated similarly. To simplify the problem, local axes on $A,B,C,D$ are taken as follows. For each atom $A$, $B$, $C$, or $D$, we consider an axial displacement ($u_{\parallel}^{A}$) along the (111) direction connecting this atom to the center 0 of the cube and two other ones ($u_{\perp 1}^{A},u_{\perp 2}^{A}$) in orthogonal directions. Due to the local $C_{3v}$ symmetry, the two orthogonal directions are equivalent. Therefore, $E_0^*$ can be simply written

$$E_0^*=\tfrac{1}{2}\sum_{i=A,B,C,D}\{k_{\parallel}(u_{\parallel}^{i})^2+k_{\perp}[(u_{\perp 1}^{i})^2+(u_{\perp 2}^{i})^2]\} , \tag{18}$$

where $k_{\parallel}$ and $k_{\perp}$ are the effective force constants for, respectively, the parallel and perpendicular directions. The total elastic energy then becomes

$$E=\delta E(\mathbf{R}_{\alpha},\underline{u}_0)+E_0^*(\underline{u}_0) , \tag{19}$$

where $\delta E$ is the energy characteristic of the coupling of the two As with their four neighbors and of the interaction between the two As. For this we use a valence-force-field model where the elastic energy takes the form given by Eq. (1).

The next step in the calculation consists in a minimization of this total elastic energy with respect to the 18 unknown (bond lengths, angles, and displacements of the four neighbors). We use radial and angular force constants derived from the bulk properties of GaAs (Ref. 22) and elemental As (Ref. 23) (this is discussed in detail in the Appendix). These turn out to be quite similar for both materials. The effective force constants are given in Ref. 19 from a Green's-function calculation for the Si vacancy (values for GaAs should be scaled by about 80% but we have checked that the atomic positions are relatively insensitive to changes in these values). The numerical values that we have used are

$$\begin{aligned}
&k_{\parallel}=1.25\ \mathrm{eV/\AA^2} ,\\
&k_{\perp}=2.35\ \mathrm{eV/\AA^2} ,\\
&k_{\theta,\alpha}=0.30\ \mathrm{eV/\AA^2} ,\\
&k_{r,B}=6.44\ \mathrm{eV/\AA^2} .
\end{aligned} \tag{20}$$

These are uncertain by about 20% but this cannot affect the conclusion of the work. The absolute minimum energy configuration is pictured in Fig. 1(b). It corresponds to a lowering of symmetry (but symmetries remain). Atomic positions of the As and the neighbors are given in

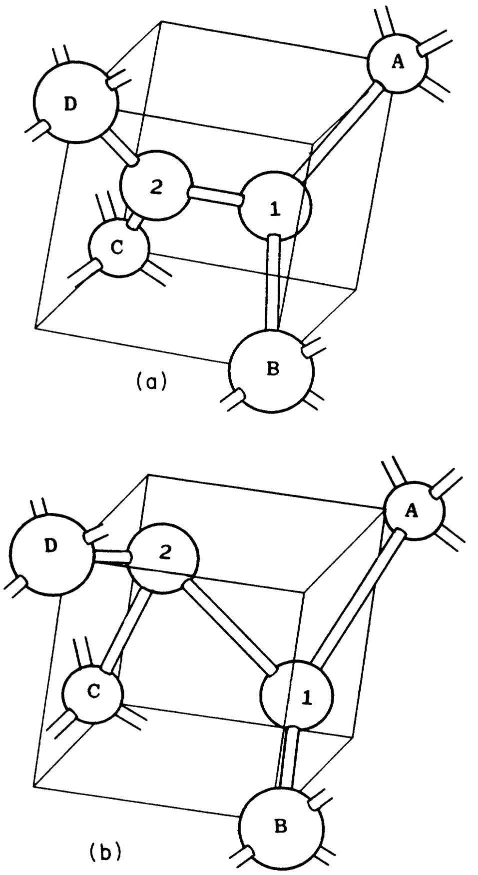

FIG. 1. Local atomic structure of the split interstitial (a) with no lattice relaxation and (b) the calculated asymmetric situation. In case (a), the coordinates of the four neighbors are $A$, (+ 1.40, + 1.40, + 1.40 ) Å; $B$, (+ 1.40, − 1.40, − 1.40) Å; $C$, (− 1.40, + 1.40, − 1.40) Å; and $D$, (− 1.40, − 1.40, + 1.40) Å. In case (b) the coordinates of the two central atoms are (±0.89,0.69, ∓0.70) Å while the displacement coordinates of $A$ and $C$ are (±0.30,0.11, ∓0.018) Å and those of $B$ and $D$ are (±0.15, ∓0.064, ∓0.037) Å.

Fig. 1(b) (the origin of the axes being the center of the cube). This configuration is compatible *a posteriori* with the assumption made for the calculation. Each As has only three first neighbors ($d_{12}=2.27$ Å, $d_{1A}=d_{1B}=d_{2C}=d_{2D}=2.38$ Å, $d_{1C}=d_{2A}=2.80$ Å, and $d_{1D}=d_{2B}=3.91$ Å). As will be discussed later, the obtained asymmetric configuration results mainly from the importance of $k_{r,B}$ compared to $k_{\theta,\alpha}$: this explains why bond lengths are not far from the bulk ones. Thus the bond angles can differ a little more from their perfect lattice references (the angles are 74°, 114°, 118° around an As and are 80°, 118°, 115° around a neighbor). Nevertheless, deviations from 97° and 109° are small enough to justify the use of expression (1).

We found a total elastic energy of 2.3 eV: this value is sufficiently low to expect that such an atomic configuration effectively is metastable, provided that it corresponds to covalent bonds of course. The following step is then to perform an electronic structure calculation for the atomic configuration of Fig. 1(b).

## IV. GREEN'S-FUNCTION CALCULATION OF THE ELECTRONIC STRUCTURE OF THE 0* STATE

We present here a Green's-function calculation of the electronic structure of the As pair in the 0* state. This is done in a tight-binding approach. All the atoms are described classically by one "*s*" and three "*p*" orbitals. We first calculate the Green's functions for the perfect GaAs crystal. The Hamiltonian in the basis of the Bloch states is obtained by the procedure described in Ref. 24: interactions up to second nearest neighbors are determined from a fit to the band structure. Green's functions are derived by integration over the Brillouin zone[25] as it has been done for Si (Ref. 26). The second step consists of the removal of a Ga atom to create the vacancy: the latter is simulated by an infinite potential on the Ga site as is described in Ref. 27.

Then the As pair is introduced and coupled to the crystal with the vacancy. This coupling is performed using Dyson's equation

$$G=G_0+G_0VG\ , \qquad (21)$$

where $G_0$ is the Green's function of the bulk crystal with the vacancy, $G$ is the final Green's function, and $V$ is the matrix of the perturbation induced by the defect. As usual, the local density of states on an orbital $i$ is obtained using the following relation:

$$n_i(E)=-\frac{1}{\pi}\mathrm{Im}[G_{ii}(E)]\ , \qquad (22)$$

where $G_{ii}(E)$ is the diagonal Green's-function element on the orbital $i$.

The interatomic terms of the perturbation matrix $V$ for the metastable configuration of Fig. 1(b) are deduced from Harrison's rules as given in Ref. 28 for nearest-neighbors interactions (each interstitial As has three nearest neighbors, at a distance 2.27 Å for the second As of the pair and 2.38 Å for the two others). We also include the influence of close second nearest neighbors at a distance 2.8 Å for which we consider the interactions to be reduced by a factor of 2 with respect to nearest neighbors. This reduction is more important than the one predicted by Harrison's rules.[28] This is justified by the fact that the empirical rules are no more valid for longer distance. Recently, the following law for the second nearest-neighbor interactions has been successfully used:[29]

$$V(d)=V(d_0)\exp\left[-2.5\left[\frac{d}{d_0}-1\right]\right]\ , \qquad (23)$$

where $V(d)$ is the second neighbor interaction at distance $d$ and $d_0$ is the first neighbor distance. This rule is equally justified in Ref. 30. In our case ($d_0=2.27$ Å and $d=2.8$ Å), this relation leads to a reduction factor close to 2.

The important relaxation of the four neighbors of the pair (see Sec. III) from their perfect lattice position surely modifies the local electronic density. In our calculation, we do not calculate explicitly the positions of the backbond atoms of $A,B,C,D$. These will move in such a way that the angles will be as close as possible to the perfect tetrahedral angles. In terms of the $sp^3$ hybrids belonging to $A,B,C,D$, this means that one of them (i.e., the dangling bond if atoms 1 and 2 are removed) will point from the displaced atom $A$, $B$, $C$, or $D$ towards its neighboring As 1 or 2. To take this effect into account, we have thus determined $G_0$ on $A$, $B$, $C$, and $D$ by imposing a rigid rotation on the unperturbed vacancy matrix such that the dangling bond hybrids are correctly oriented.

Finally, approximate self-consistency is achieved. As discussed in Ref. 31, we use a local charge-neutrality condition corresponding to a very efficient screening. The "*s*" and "*p*" orbital energies ($E_s,E_p$) of each As of the pair are given by

$$\begin{aligned} E_s&=E_{s0}+\Delta E\ ,\\ E_p&=E_{p0}+\Delta E\ , \end{aligned} \qquad (24)$$

where $E_{s0}$ and $E_{p0}$ are the As bulk energies given in Ref. 24 (respectively, $-6.72$ and 0.64 eV) and $\Delta E$ is a common shift adjusted in such way that each As is neutral (five electrons). A potential $\Delta V$ is also applied on the four neighbors to assure the global neutrality of the cell composed by the six As. We obtain $\Delta E=-1.81$ eV and $\Delta V=-0.74$ eV. The total ("*s*" + "*p*") local density of states on the six As is plotted in Fig. 2 and the partial "*s*" density in Fig. 3. The absence of gap levels is in agreement with existing experimental evidence. This implies that the defect only exists in one charge state found to be the + one (this will be discussed in the next section) which precisely corresponds to the quenchable charge state of the 0 configuration,[6,8] in agreement with the fact that the charge state does not change in the $0\rightarrow0^*$ transformation. The local "*s*" density in Fig. 3 clearly shows that "*s*" states are present mainly in the valence band as expected in a molecular model (see Sec. V). We find again a very covalent situation (Fig. 2) since there is no level lying in the proximity of the band gap (strong interaction). This situation gives us confidence in our cal-

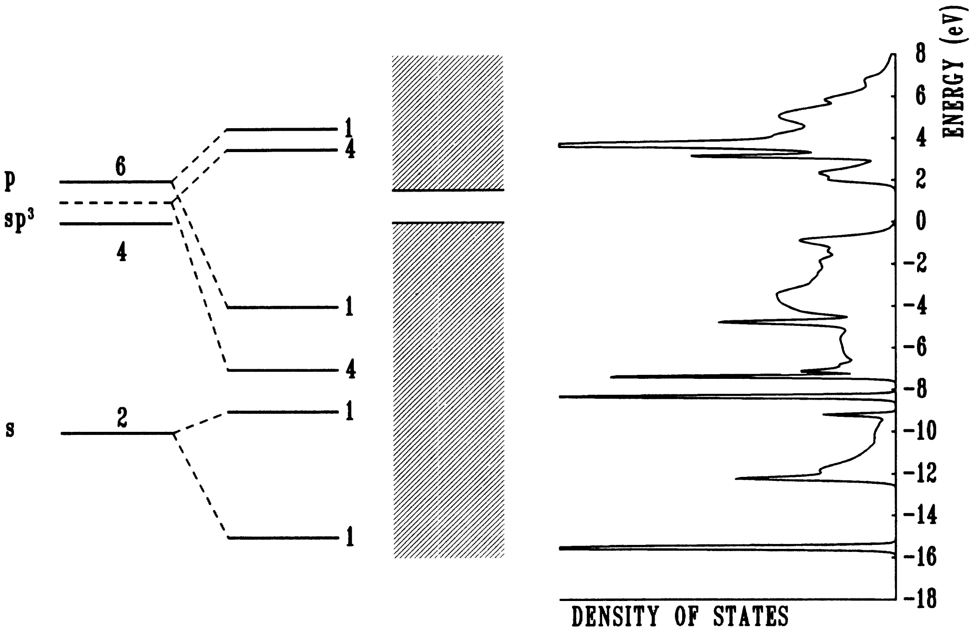

FIG. 2. (a) Schematic level scheme in the molecular model of the split interstitial with respect to the band gap (the numbers indicate the degeneracy of the levels). (b) Local density of states on one of the two central As atoms in the configuration of Fig. 1(b).

culation because modifications of our parameters or of our self-consistency procedures will not change the main conclusions (for example, we have observed that the rotations previously described are not fundamental). Strong peaks can be assigned to bonding and antibonding states as in a simple molecular model.

## V. DISCUSSION OF THE RESULTS

In this section, we analyze the numerical results obtained above (both for the elastic and electronic calculations) on the basis of simple models. This will allow us to understand the physical origin of the results and will, in some way, confirm their validity.

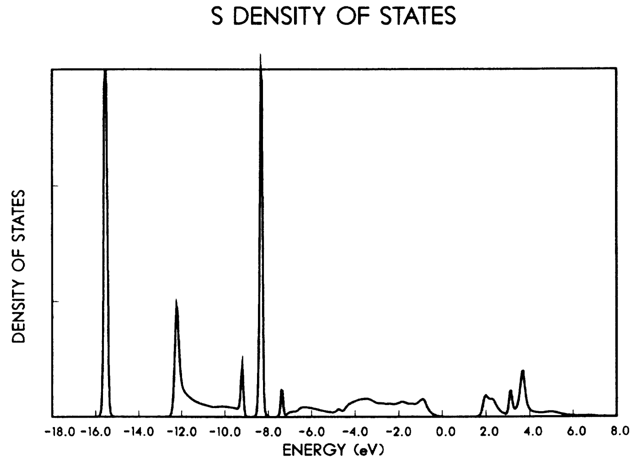

FIG. 3. Local "*s*" density of states on one of the two central As atoms in the configuration of Fig. 1(b).

Let us then first consider the problem of finding the minimum atomic configuration for the metastable state. Our simplified description will be based on the fact that in the valence-force-field expression (1) of the elastic energy the angular force constants $k_\theta$ are much smaller than the radial force constants $k_r$, as shown by Ref. 19. The most trivial simplification then consists of taking $k_\theta = 0$ as a zeroth-order approximation. We also kept the four neighbors $A,B,C,D$ of Fig. 1(a) fixed at their perfect lattice positions. In searching for the corresponding minimum energy configuration, one can wonder if the elastic energy can reach its lowest possible bound, i.e., zero. This would also mean that all interatomic distances of the cluster of Fig. 1 are equal to the corresponding bulk material bond length. As this one is practically the same in crystalline GaAs (2.43 Å) and in As (2.49 Å), we search for solutions where any of the five bonds of Fig. 1 has the same bond length as in GaAs. Calling $x_1, y_1, z_1$ and $x_2, y_2, z_2$ the coordinates of the two As atoms in units of the bulk GaAs bond length, we easily end up with the following equations to be fulfilled:

$$\begin{aligned} &x_1 = -y_1 , \quad x_2 = y_2 , \\ &2x_1^2 + (z_1 + 1/\sqrt{3})^2 = \tfrac{1}{3} , \\ &2x_2^2 + (z_2 - 1/\sqrt{3})^2 = \tfrac{1}{3} , \\ &2x_1^2 + x_2^2 + (z_1 - z_2)^2 = 1 . \end{aligned} \tag{25}$$

The last three of Eqs. (25) concern four unknowns. We can thus impose one extra condition; we choose this one to be

$$z_1=-z_2 \tag{26}$$

which preserves some symmetry for the system. This directly imposes $x_2=-x_1$ from (25). Injecting these conditions into (25) gives

$$z_1=-0.37,\quad x_1=0.38\ . \tag{27}$$

One can check easily that this minimum configuration is in fact close to what was found numerically before. Introduction of the angular terms will simply push the four neighbors outward and will only slightly affect the atomic arrangement.

As regards the electronic structure, one can build a simple molecular model as for GaAs or As based on a tight-binding description of the defect. The two As of the pair are each represented by one "*s*" and three "*p*" atomic orbitals. These orbitals interact mainly with the four $sp^3$ hybrid orbitals of the four neighbors pointing towards the two As. Due to the important difference between the "*s*" and "*p*" energies ($\approx 8$ eV), we can treat "*s*" states separately. The interaction between "*s*" orbitals and the other atoms leads to bonding and antibonding "*s*" states lying deeply in the valence band (see Fig. 3).

For the remaining orbitals (six As "*p*" and three $sp^3$ hybrids), we can adopt the following simplified point of view (see Fig. 4). If bond angles around the As of the pair were equal to 90° and if the $sp^3$ hybrids point towards the interstitial As along the bonds, the orbitals interact mainly by pairs so that there would be four $sp^3$—$p$ bonds and one $p$—$p$ bond along the axis between the two As. These bonds are very covalent so that we expect the bonding-antibonding splitting to be larger than the GaAs gap (see Fig. 2). Therefore this electronic structure is mainly characterized by the absence of gap states. Moreover, the split-interstitial corresponds to a positive charge state since a neutral defect would contain 15 electrons (five on the $sp^3$ hybrids of the Ga vacancy and five per As atom of the pair). Obviously, the use of the atomic configuration obtained previously complicates the description of the electronic structure. There will be mixings between the various orbitals but we can expect that the main conclusions remain valid. The complete calculation of the electronic structure performed before confirms this simple picture.

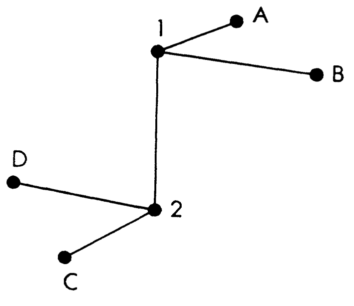

FIG. 4. Simplified model for the atomic structure of the As pair allowing the simple molecular description of the electronic structure of Fig. 2(b). Bonds between the six As are taken perpendicular as in amorphous As.

## VI. SUMMARY AND CONCLUSIONS

In this work, we have proposed and justified theoretically an atomic configuration model for the metastable state of the *EL*2 center. The electronic structure of the split-interstitial fulfills the experimental requirements. This defect is characterized by the absence of gap levels and is in the + charge state. Consequently, according to Ref. 12 and the above discussion, we can associate the 0 state with the $\mathrm{As_{Ga}}$-$\mathrm{As}_i$ pair at about 1.5 bond-length distance and the 0* state with the split-interstitial pair. The paramagnetic state of 0 is $0^{2+}$, corresponding to $\mathrm{As_{Ga}}^+$-$\mathrm{As}_i{}^+$; its quenchable state $0^+$ is $\mathrm{As^0_{Ga}}$-$\mathrm{As}_i{}^+$ which, by optical excitation around 1.1 eV, should then be transformed into our proposed split-interstitial $(0^*)^+$ metastable configuration.

## APPENDIX

We discuss here the numerical values of the force constants $k_r$ and $k_\theta$. For GaAs, the Keating model used by Martin gives[22]

$$k_r=7.99\ \mathrm{eV/\mathring{A}^2},\quad k_\theta=0.37\ \mathrm{eV/\mathring{A}^2}\ . \tag{A1}$$

This model is not strictly equivalent to the valence-force-field model used here but the two force constants should be close to those given by (A1).

A discussion for *a*-As can be made very easily in terms of a simple model. First, the infrared absorption spectrum of *a*-As consists of a dominant and relatively sharp band at $\sim 230\ \mathrm{cm}^{-1}$ and relatively weak secondary structures.[23] To get some feeling of the value of $k_r$ in this material let us idealize this material by assuming that the bond angles are 90° instead of ~97° and that we first neglect $k_\theta$. On each atom, we can thus define three orthonormal displacements directed along each bond. Such displacements will couple by pairs within each bond. Let us call $u_{ij}$ and $u_{ji}$ the displacements involved in the stretching in the bond connecting atoms $i$ and $j$. Clearly the combination $(u_{ij}+u_{ji})/\sqrt{2}$ leads to no stretching at all and corresponds to a mode of zero frequency. On the other hand $(u_{ij}-u_{ji})/\sqrt{2}$ corresponds to pure stretching and a potential energy equal to $k_r(u_{ij}-u_{ji}/\sqrt{2})^2$. Such a mode gives rise to a vibration frequency

$$\bar{\omega}=\left[\frac{2k_r}{M}\right]^{1/2}, \tag{A2}$$

where $M$ is the As atomic mass. Thus the vibrational density of states in our idealized description corresponds to two delta functions of equal weight at $\omega=0$ and $\bar{\omega}$. Inclusion of $k_\theta$ will broaden and slightly shift these two lines. As discussed in Ref. 23, the ratio $k_\theta/k_r$ is again very small so that one gets a good order of magnitude of $k_r$ by identifying $\bar{\omega}$ with the main line at $230\ \mathrm{cm}^{-1}$. This leads to $k_r \sim 6.44\ \mathrm{ev/\mathring{A}^2}$. The bonds considered in Fig. 1 are As-As bonds and as the $k_r$ for GaAs and elemental As are close enough, we have decided to use this value in Ref. 19. For $k_\theta$, we have taken a value similar to the one occurring in GaAs but our results are not very sensitive to $k_\theta$ provided it remains small compared to $k_r$.

[1] For a recent review on this defect, see, for instance, S. Makram-Ebeid, P. Langlade, and G. M. Martin, in *Proceedings of the Third Conference on Semi-Insulating III-V Materials, location, 1985,* edited by D. C. Look and J. S. Blakemore (Shiva, Nantwich, England, 1985), p. 184.

[2] H. J. Von Bardeleben and J. C. Bourgoin, in Proceedings of the Fifth International "Lund" Conference on Deep Level Impurities in Semiconductors, St. Andrews, Scotland, June, 1985 (unpublished).

[3] H. J. Von Bardeleben, D. Stievenard, J. C. Bourgoin, and A. Huber, Appl. Phys. Lett. **47**, 970 (1985).

[4] H. J. Von Bardeleben, D. Stievenard, J. C. Bourgoin, A. Huber, and J. C. Bourgoin, Phys. Rev. B **34**, 7192 (1986).

[5] B. K. Meyer, D. M. Hofmann, and J. M. Spaeth, in *Defects in Semiconductors,* Vols. 10–12 of *Materials Science Forum,* edited by H. J. Von Bardeleben (Trans Tech, Switzerland, 1986), p. 311.

[6] B. K. Meyer, D. M. Hofmann, J. R. Niklas, and J. M. Spaeth, Phys. Rev. B **36**, 1332 (1987).

[7] G. A. Baraff and M. Lannoo, Rev. Phys. Appl. **23**, 817 (1988).

[8] J. C. Bourgoin and M. Lannoo, Rev. Phys. Appl. **23**, 863 (1988).

[9] E. R. Weber and J. Schneider, in *Proceedings of the 12th International Conference on Defects in Semiconductors, Amsterdam, 1982,* edited by C. A. J. Ammerlaan [Physica **116B+C**, 398 (1983)].

[10] G. A. Baraff and M. Schlüter, Phys. Rev. B **33**, 7346 (1986).

[11] M. Lannoo, Phys. Rev. B **36**, 9355 (1987).

[12] G. A. Baraff, M. Lannoo, and M. Schlüter (unpublished).

[13] G. Vincent and D. Bois, Solid State Commun. **27**, 431 (1978).

[14] D. Stievenard, H. J. Von Bardeleben, J. C. Bourgoin, and A. Huber, in *Defects in Semiconductors,* Ref. 5, p. 305.

[15] H. J. Von Bardeleben, J. C. Bourgoin, D. Stievenard, and M. Lannoo (unpublished).

[16] C. Delerue, M. Lannoo, D. Stievenard, H. J. Von Bardeleben, and J. C. Bourgoin, Phys. Rev. Lett. **59**, 2875 (1987).

[17] G. A. Baraff and M. Schlüter, Phys. Rev. B **35**, 6154 (1987).

[18] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980).

[19] M. Lannoo and G. Allan, Phys. Rev. B **25**, 4089 (1982).

[20] G. Picoli, A. Chomette, and M. Lannoo, Phys. Rev. B **30**, 7138 (1982).

[21] J. N. Decarpigny, Rev. Phys. Appl. **15**, 661 (1980).

[22] R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

[23] G. Lucovsky and J. C. Knights, Phys. Rev. B **10**, 4324 (1974).

[24] D. N. Talwar and C. S. Ting, Phys. Rev. B **25**, 2660 (1982).

[25] J. Bernholc and S. T. Pantelides, Phys. Rev. B **18**, 1780 (1978).

[26] J. Petit, G. Allan, and M. Lannoo, Phys. Rev. B **33**, 8595 (1986).

[27] M. Lannoo and P. Lenglart, J. Phys. Chem. Solids **30**, 2409 (1969).

[28] W. A. Harrison, Phys. Rev. B **24**, 5835 (1981).

[29] I. Lefebvre, M. Lannoo, G. Allan, A. Ibanez, J. Fourcade, J. C. Jumas, and E. Beaurepaire, Phys. Rev. Lett. **52**, 2471 (1987).

[30] G. Allan and M. Lannoo, J. Phys. (Paris) **44**, 1355 (1983).

[31] C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **33**, 7386 (1986).