Isolated As antisite in GaAs: Possibility of the *EL2* defect

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A theoretical treatment of the properties of the isolated As antisite in GaAs is presented. The results are compared to recent works of Dabrowski and Scheffler and of Chadi and Chang, which suggested that the As antisite be identified with the *EL2* defect in GaAs. A large supercell, an extensive plane-wave basis, and several Brillouin-zone sampling points are used to improve the accuracy of theoretical predictions. We find that the isolated antisite exhibits metastability, which is the most important property of the *EL2* defect, but the energy barrier is lower from the experimental value by a factor of 2. Possible sources of the discrepancy are discussed.

The *EL2* defect in GaAs is one of the most interesting and extensively studied defects in semiconductors.[1] It is a technologically important intrinsic defect because it is identified with the midgap level in semi-insulating undoped GaAs.[2] The *EL2* defect exhibits unusual behavior when exposed to light: a metastable state which is electronically passive is obtained. The defect can return from the metastable to its equilibrium state by thermal treatment. The experimentally determined optical excitation energy is 1.0–1.3 eV,[3] whereas the barrier for returning from the metastable to the equilibrium state is 0.34 eV.[4,5]

Several microscopic models have been proposed to explain this intriguing behavior.[6–14] The simplest one is the isolated As antisite, i.e., an As atom residing at a site of the Ga sublattice.[6] This defect, although very common in bulk GaAs, was believed to be too simple to account for *EL2*, in the sense that its structure did not allow for a metastable state.[15] Two recent theoretical studies indicated that the As antisite may indeed exhibit metastability.[16,17] In Ref. 16, however, no atomic relaxations were taken into account, which can alter the shape of the total-energy surface, possibly changing the metastable configuration to unstable. In Ref. 17, on the other hand, a very small supercell of 18 atoms was used for the first-principles calculations, and C_{3v} symmetry was imposed (not present in the *equilibrium* configuration), which could also affect the shape of the total-energy surface. These limitations suggested the need for a more extensive study.

In this paper we present first-principles calculations for the structural and electronic properties of the isolated As antisite, which exceed in scope previous theoretical work. Our results are in agreement with the claims of Dabrowski and Scheffler[16] (DS) and of Chadi and Chang[17] (CC), namely that the isolated As antisite exhibits a metastable state and its electronic properties are compatible with the experimental signature of *EL2*. Comparison with experiment is not completely satisfactory, however, which may be due, in part, to intrinsic limitations of the theoretical approach.

The calculations are performed in the framework of pseudopotential local-density-functional theory[18] with a plane-wave basis. We use a large supercell containing 54 atoms which is a multiple of the fcc unit cell in each translational direction, thus no particular symmetry is imposed. Each configuration is fully relaxed according to Hellmann-Feynman forces. We include plane waves with kinetic energy up to 9 Ry (corresponding to 3600 plane waves) and eight sampling points in the Brillouin zone (BZ). With these parameters, we estimate that energy differences quoted are converged to about 0.02 eV.

The most important feature for an *EL2* candidate is to demonstrate the existence of a metastable state. In the case of the As antisite, a possible metastable state may be reached by moving the As antisite along the [111] direction, away from one of its four As nearest neighbors and toward the other three. When the displaced atom reaches a position slightly beyond the plane of its three closest neighbors, a favorable, low-energy configuration may be possible, in which two As atoms are threefold bonded. An energy barrier between this potential low-energy configuration and the equilibrium configuration may be expected at the point where the As antisite crosses the plane of its three nearest neighbors. The possible barrier and metastable configurations are shown schematically as insets in Fig. 1 (labeled *B* and *M*, respectively). Figure 1 also shows the total energy of the system as the As antisite is displaced from its equilibrium position, along the path described above, neglecting atomic relaxation. The total-energy curve indicates that the an-

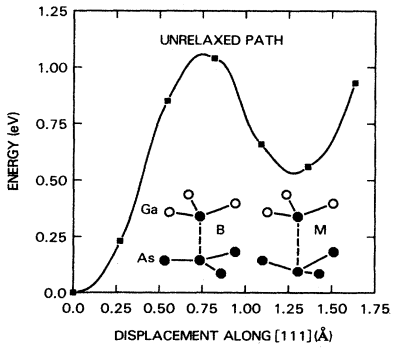

FIG. 1. Total energy as a function of displacement of the As antisite along the [111] axis. No relaxation is included along the path. The zero of energy is the relaxed equilibrium configuration. Squares are calculated points, line is spline fit. Insets are schematic representations of the barrier (*B*) and metastable (*M*) configurations.

ticipated barrier and metastable states indeed exist.

In Fig. 2 we show the valence charge density for the relaxed equilibrium configuration and the relaxations of the first and second neighbors of the antisite. The relaxed metastable state is found to have an energy of $E_M = 0.34$ eV with respect to the equilibrium state. A plot for the valence charge density and the atomic relaxations of the metastable configuration is given in Fig. 3. Comparison of the charge-density contours in Figs. 2 and 3 shows that one of the As—As bonds is broken when the antisite is displaced from the equilibrium to its metastable configuration. The energy barrier is a more difficult quantity to calculate: the relaxed saddle-point configuration is not dictated by any symmetry, but must be determined by a search over a large region of configuration space, an extremely demanding computational task. For practical reasons we take the As antisite to be frozen at the center of the triangle defined by three of its neighbors in the relaxed equilibrium configuration and allow all other atoms to relax. The energy of this configuration is a *lower bound* for the saddle-point energy and is $E_B = 0.50$ eV with respect to the equilibrium configuration. Thus the energy barrier for returning from the metastable to the equilibrium configuration has a lower bound of $E_B - E_M = 0.16$ eV. A plot of the valence charge density and the atomic relaxations for the barrier configuration is given in Fig. 4. The residual

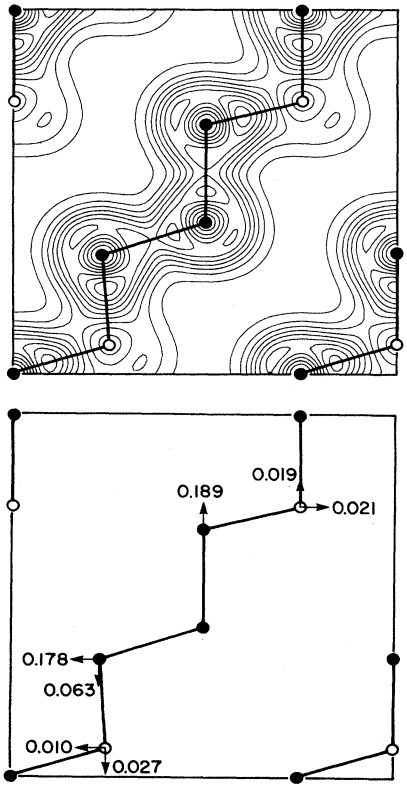

FIG. 2. Valence charge density on a (110) plane of the crystal for the equilibrium configuration. Relaxation is shown on the lower panel as displacements of atoms from ideal crystal positions in Å (arrows indicate direction only). Open circles represent Ga atoms, solid circles As atoms.

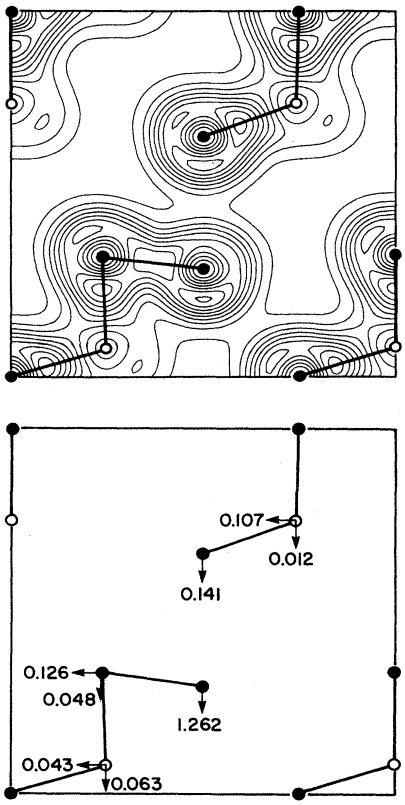

FIG. 3. Same as Fig. 2 for the metastable configuration.

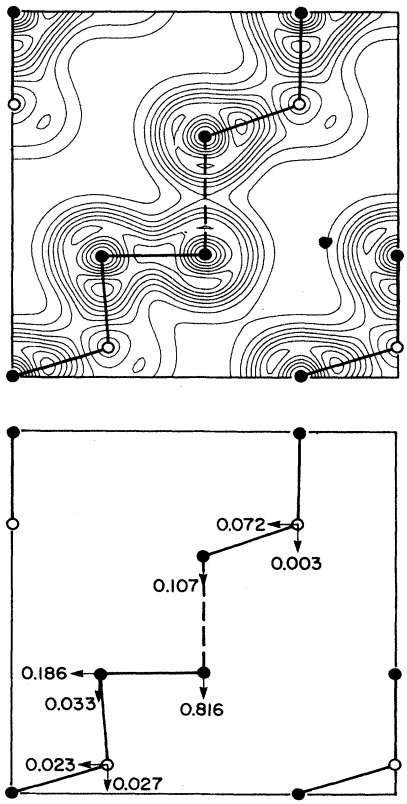

FIG. 4. Same as Fig. 2 for the barrier configuration.

forces on the frozen antisite were found to be very small, indicating that the position we chose lies very close to the true saddle point (where the forces must vanish); consequently, our lower-bound estimate must be very close to the true value of the energy barrier.

In Table I we compare our values for the energy and the structural characteristics of the different configurations to the results of other calculations and to experiment. The neglect of relaxation by DS gives a much larger energy barrier of 0.92 eV (these authors estimate from elastic constants that relaxation brings the energy barrier down to 0.4–0.5 eV). The first-principles results in the smaller supercell of CC give slightly higher values both for the energy of the metastable configuration ($E_M = 0.38$ eV) and for the energy barrier ($E_B - E_M = 0.20$ eV). Our calculated energy barrier is smaller than the experimentally observed energy barrier by a factor of 2. This may be due to finite-size effects, to convergence limits (number of plane waves in the basis set or number of BZ points), or to the approximate position of the frozen antisite at the barrier configuration. At present, it is not feasible to improve any aspect of the calculation.

We examine next the electronic properties of the isolated antisite in order to compare it to the $EL2$ defect. It is known that the band gap for bulk GaAs is given only to 50% accuracy in the formalism employed here.[19] This limitation may also affect the value of the energy barrier, which is determined by the position of states in the band gap. With the convergence parameters mentioned above, we fortuitously obtain a band gap equal to the experimental value (1.5 eV) at the theoretically determined lattice constant of GaAs, which is 5.564 Å (1.5% smaller than the experimental value). In the following, the positions of defect states in the band gap will be taken as the weighted average of the band energy at the specific BZ points included in the calculation and their dispersion (due to the finite size of the supercell) will be indicated by error bars.

One important electronic excitation energy is the energy difference between the occupied and unoccupied defect states in the equilibrium configuration. This energy is associated with the optical internal excitation.[16] Assuming that the optical excitation takes place at Γ, we calculate an excitation energy of 1.22 eV, which is close to the result of DS and compares very favorably with experiment (see Table I). A second important aspect is the position of states in the gap and the character of their wave functions, which is crucial in explaining the optical bleaching of $EL2$. We find that the equilibrium configuration has a fully occupied state near midgap, at 0.9 ± 0.4 eV above the valence-band maximum (VBM). This compares well with experiment and with the results of DS (see Table I). The wave function of this state is centered at the As antisite [Fig. 5(a)] and is well localized. In the metastable configuration there are two states in the gap, one close to the VBM (0.2 ± 0.1 eV above) and another close to the conduction-band minimum (CBM) (0.3 ± 0.2 eV below). The wave functions of these two states are also well localized and have very little overlap: one is associated with the Ga-bonded threefold-coordinated As atom [Fig. 5(b)] and the other is associated with the displaced As antisite [Fig. 5(c)]. The vanishingly small overlap between these states and their large separation in energy (> 1 eV) lead to an electrically passive metastable configuration, in agreement with experimental observations. For comparison, at the metastable configuration, DS find only one state in the gap at 0.3 eV above the VBM (the other defect state lies above the CBM), whereas CC find two states, one 0.2 eV above the VBM and the other 0.5 eV below the CBM (see Table I). Other properties of the isolated antisite, e.g., its symmetry (C_{3v} in the *metastable* configuration) and charge state (neutral in both the equilibrium and metastable configurations) are also in agreement with experimental observations[20,21] (for detailed discussions, see Refs. 16 and 17).

In conclusion, we have presented a theoretical treatment of the properties of the isolated As antisite in GaAs. Our results are compared to previous theoretical work

TABLE I. Theoretical results for the isolated As antisite in GaAs and available experimental data for $EL2$ (energies are in eV).

	DS (Ref. 16)	CC (Ref. 17)	This work	Experiment
Metastable state energy	0.13	0.38[a]	0.34	
Energy barrier	0.92	0.20[a]	0.16	0.34[b]
Displacement along [111] (Å)	1.4	1.2	1.3	
Optical excitation energy	0.97		1.22	1.18[c]
		Gap states		
Equilibrium configuration occupied (above VBM)	0.6		0.9 ± 0.4[d]	0.7[e]
Metastable configuration occupied (above VBM)	0.3	0.2 ± 0.1	0.2 ± 0.1[d]	
unoccupied (below CBM)		0.5	0.3 ± 0.2[d]	

[a]For consistent comparison, only first-principles results of Ref. 17 are quoted.
[b]References 4 and 5.
[c]Reference 3.
[d]Position of state is the average of the band energy at eight BZ points. Error bars are due to finite-size effects which give band dispersion.
[e]Reference 2 (for a gap of 1.52 eV).

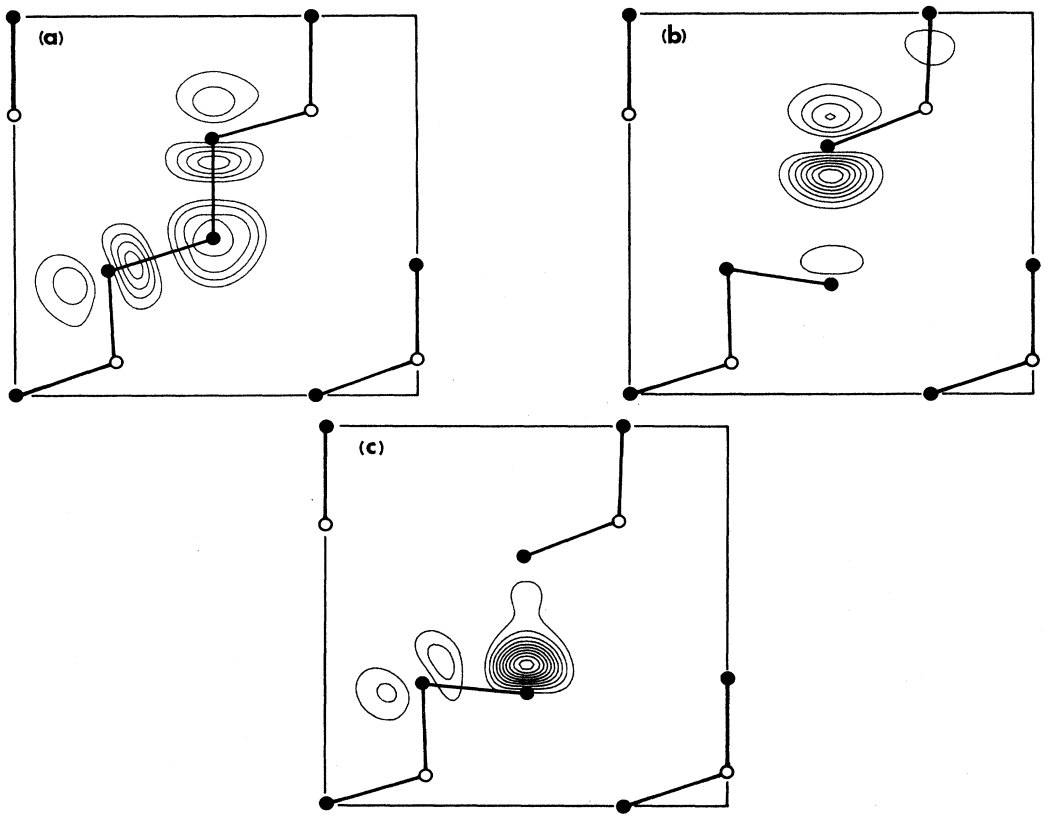

FIG. 5. Charge density of gap states. (a) Occupied midgap state of the equilibrium configuration. (b) Occupied state of the metastable configuration. (c) Unoccupied state of the metastable configuration.

which suggested that the As antisite be identified with the $EL2$ defect.[16,17] The use of a large supercell, an extensive plane-wave basis, and several BZ sampling points in the present work, as well as inclusion of full atomic relaxation, give improved theoretical estimates for the properties of the As antisite. We find that a metastable state exists and is separated from the equilibrium configuration by an energy barrier smaller by a factor of 2 from the experimental values. This level of agreement with experiment may be due to intrinsic limitations of the theoretical approach or to the need for further search for an $EL2$ model.

[1]See, e.g., the review article by G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986).
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