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Tight-binding molecular-dynamics study of point defects in GaAs

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Tight-binding molecular-dynamics simulations at 0 K have been performed in order to study the effect of defects (vacancies and antisites) in different states of charge on the electronic and structural properties of GaAs. Relaxations are fully included in the model, and for each defect we calculate the local atomic structure, the volume change upon relaxing, the formation energy (including chemical potential contributions), and the ionization levels. We find Ga vacancies to relax by an amount which is independent of the state of charge, consistent with positron lifetime measurements. Our calculations also predict Ga vacancies to exhibit a negative-U effect, and to assume a triply negative charge state for most values of the electron chemical potential. The relaxation of As vacancies, on the contrary, depends sensitively on the state of charge. The model confirms the two experimentally observed ionization levels for this defect, just below the conduction-band minimum. Likewise, Ga antisites exhibit large relaxations. In fact, in the neutral state, relaxation is so large that it leads to a "broken-bond" configuration, in excellent accord with the first-principles calculations of Zhang and Chadi [Phys. Rev. Lett. **64**, 1789 (1990)]. This system also exhibits a negative-U effect, for values of the electron chemical potential near midgap. For As antisites, we find only a weak relaxation, independent of the charge. The model predicts the neutral state of the defect to be the ground state for values of the electron chemical potential near and above midgap, which supports the view that the $EL2$ defect is a neutral As antisite. Upon comparing the formation energies of the various defects we finally find that, for all values of the atomic chemical potentials, antisites are most likely to occur than vacancies.

I. INTRODUCTION

Various types of defects form during the growth of crystals. For semiconductors, defects strongly affect the electrical and optical properties, since they interact with free carriers by acting as traps or scattering and recombination centers.[1,2] However, the microscopic structure of defects, and even their identification, are still largely unresolved. One common technique to study the structure of defects in semiconductors, electron paramagnetic resonance (EPR),[1] often gives signals difficult to analyze, especially in materials where the isotopes all have the same spin (such as GaAs), in which case the hyperfine structure of the spectra cannot be resolved even with high-resolution techniques.

Another useful tool for probing defects on the atomic scale is positron annihilation.[2–5] Positrons in solids are strongly repelled by positive ions, while they annihilate with electrons. In the open volume (OV) associated with a vacancy, the electron density is reduced compared to defect-free regions of the crystal and, as a result, the lifetime of the positron is larger (i.e., it is trapped by the vacancy). The OV of the vacancy, further, changes with its state of charge, and the lifetime of the trapped positron changes correspondingly. Thus, from a careful analysis of positron lifetimes, the identity of the various defects, as well as their ionization levels (values of the electron chemical potential at which the charge state changes), can in principle be determined. A detailed interpretation of positron annihilation measurements is, however, not easy in compound semiconductors such as the III-V's,[2–4] which can have vacancies of two kinds (anion and cation) in different charge states. Proper identification of vacancies in these materials has been a subject of concern for several years.[2–5]

The influence of native point defects on the electrical and optical properties of GaAs is known to be very important. For example, in view of its technological relevance, the so-called $EL2$ defect[6–14] has been the object of extensive theoretical and experimental studies. This defect, indeed, can compensate residual acceptor impurities and pin the Fermi level at midgap; thus, GaAs can be manufactured without intentional impurity doping. On the basis of recent measurements,[6–9,14] the $EL2$ defect has been related to the As antisite (i.e., the substitution of a Ga by an As in the otherwise perfect structure); however, it is not clear whether the As antisite exists as an isolated defect or if it is part of a larger complex. In contrast, very little is known about the Ga antisite.[15]

There have been a number of theoretical studies[12,16–20] of point defects in GaAs. In most cases, however, the full relaxation of both electronic and ionic degrees of freedom was not performed, or the contribution of electronic and atomic chemical potentials not fully considered. Notable exceptions are Refs. 15 and 19; Ref. 15, however, deals with Ga antisites only for which there is no need to consider atomic chemical potential contributions, while Ref. 19 is concerned with the equilibrium concentration of defects, but does not discuss relaxation. We achieve

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both here by using an atomic model based on a tight-binding (TB) description of the electronic structure. TB total-energy models have proved a good alternative (i.e., more economical) to detailed first-principles molecular-dynamics (MD) calculations, such as in the method of Car and Parrinello,[21] at least in the case of extended-system properties (e.g., the structure of liquids and amorphous materials).

The present work serves two purposes: in addition to providing a consistent physical picture of the structure and energetics of a variety of point defects in GaAs, our calculations will be used to assess the validity of the semiempirical, bulk-fitted, TB total-energy scheme in describing reduced-symmetry geometries, i.e., transferability. Thus we have used the model to investigate single vacancies and antisites in GaAs, taking into account the full relaxation of atoms, as well as electron and atomic chemical potential contributions to the total energy. We find the model to be generally in good agreement with corresponding calculations using more accurate (in principle) *ab initio* approaches, as well as with experimental data when available. Our calculations further reveal, for Ga and As antisites and Ga vacancies, the existence of a "negative-U effect" and provide a consistent picture of positron lifetime measurements in terms of the OV's for the various charge states of the vacancies. The calculated ionization levels for As vacancies show good agreement with positron annihilation experiments, thus resolving the uncertainties concerning the identification of the observed ionization levels.[2–4] The calculated local atomic structures of the antisites agree well with both *ab initio* results[15] and scanning tunneling microscopy and spectroscopy measurements.[22] Upon comparing the formation energies of the various defects, we find that, for all values of the atomic chemical potentials, antisites are more likely to occur than vacancies.

In Sec. II we start with a brief description of the model used here, including the TB representation of the total energy, and discuss chemical potentials, whose contribution to defect formation energies can be determinant in the case of compounds. In Secs. III and IV, we present our results for vacancies and antisites, respectively. In Sec. V, we discuss the thermodynamically most favored system under different stoichiometries. A summary and concluding remarks are provided in Sec. VI.

II. COMPUTATIONAL DETAILS

In the semiempirical TB approach, the total energy is written as the sum of two terms; the "band-structure" energy,[23] which is expressed in terms of a finite number of localized atomic orbitals, and a repulsive term,[24–26] which describes the ionic repulsion at short distances, including charge-transfer effects. In the present study, we adopt the model developed by Molteni *et al.*,[27] where the TB interactions, which include only nearest neighbors, are parametrized in terms of an sp^3s^* basis set.[28,29] This model, known to give a good representation of the electronic density of states, has been used successfully to simulate the structure of liquid and amorphous GaAs.[27]

Our simulations were carried out using a 64-atom supercell,[30] from which a single atom was removed in order to study vacancies, or in which a Ga was substituted for an As, or vice versa, in order to study antisites. Periodic boundary conditions in all three Cartesian directions were used to eliminate surface effects. The TB energies were obtained by direct diagonalization of the TB matrices constructed by sampling only the Γ point in the reciprocal-space integrations. For each defect, the ground-state structure was determined by performing a full, unconstrained, relaxation of the atomic positions. The interactions were cut off at 3.4 Å. In order to gain some feeling for the accuracy of our calculations, we have carried out some test runs on a larger system consisting of 216 atoms. (This is, in a sense, equivalent to using more points in the Brillouin-zone summation.) We found, in all cases, differences in energy of less than 0.02 eV compared to the smaller system, a value, therefore, which we may take as the "error bar" on the calculated energies.

The TB scheme we use here results in a transfer of charge from Ga to As of 0.187 electrons, yielding an ionicity f_i of 0.297. This is in excellent agreement with the empirical pseudopotential model calculations of Walter and Cohen,[31] who find $f_i = 0.31$, as well as with Pauling's heat-of-formation approach to the atomic electronegativity,[32] which yields $f_i = 0.28$. In comparison, using a TB model with an sp^3 basis set but with both first and second nearest-neighbor interactions, Xu and Lindefelt[16] obtained $f_i = 0.203$. We note (this will become important below) that the present TB model[28] also predicts accurately the energy gap E_g of GaAs — 1.544 eV, compared to 1.52 eV experimentally. This is in contrast with density functional theory (DFT) in the local density approximation (LDA), which underestimates energy gaps by a factor of approximately 2; for GaAs, for instance, DFT predicts $E_g = 0.7$ eV.[20]

In order to determine the thermodynamically most favorable configuration of a compound material, where stoichiometry can vary, it is necessary to take into account the contributions to the total energy of the atomic chemical potentials. For systems in a charged state, in addition, the contribution from the electron chemical potential μ_e must also be included; the formation energy Ω of a defect in charge state Q, where Q is the number of electrons transferred from (or to) an infinite reservoir,[33] can be written[14,19,34–36]

$$\Omega = E_D[N_C, N_A] + Q(\mu_e + E_v) - N_C\mu_C - N_A\mu_A, \quad (2.1)$$

where $E_D[N_C, N_A]$ is the total energy of the supercell including the defect, N_A and N_C are the number of anions (here As) and cations (here Ga), respectively, with μ_C and μ_A the corresponding chemical potentials. In the above, μ_e is measured with respect to the top of the valence band E_v of pure bulk GaAs.

The atomic chemical potential, for a given phase, is obtained from the derivative of the Gibbs free energy,[37] $G = E+PV-TS$, with respect to the number of particles of type i, i.e., $\mu_i = dG/dn_i$; to a good approximation in the solid state[34]

$$\mu_i \approx dE/dn_i. \quad (2.2)$$

The defect formation energy Ω, further, can be expressed in terms of either the cation or the anion chemical potential by introducing the quantity $\mu_{A+C} = \mu_A + \mu_C$ (Refs. 19, 34 and 35) [which can be determined by using Eq. (2.2)] for the ground-state structure of the pure bulk compound; thus

$$\Omega[N_C,N_A] = E_D[N_C,N_A] + Q(\mu_e + E_v) - N_A\mu_{C+A} - (N_C - N_A)(\Delta\mu_C + \mu_C^b), \qquad (2.3)$$

where $\Delta\mu_C$ measures deviations of μ_C from the bulk cation chemical potential; $\Delta\mu_C = \mu_C - \mu_C^b$. $\Delta\mu_C$, for real laboratory samples, depends on conditions of preparation and satisfies $-\Delta H \leq \Delta\mu_C \leq 0$, where ΔH is the heat of formation of the compound. For GaAs, ΔH is of the order of 0.74 eV.[38] We have estimated μ_C^b, using the present TB model, and found -3.50 eV, while $\mu_{C+A} = -12.41$ eV per GaAs pair.

Defects, as noted earlier, can exist in various states of charge, whose values are *a priori* unknown. *A posteriori*, however, the values of interest can be determined by requiring the formation energies of all defects to be positive (since the zinc-blende structure is the ground state). In addition, as will become clear below, we considered here only those defects that affect ionization in the allowed range for the electron chemical potential, namely, $0 \leq \mu_e \leq E_g$ (depending, also, on preparation). The defects considered in the present work, which obey these criteria, are listed in Table I, where we also give the highest occupied state and/or one-electron gap states.

TABLE I. The highest occupied state and/or one-electron gap states for the "relevant" defects considered in the present work (see text). Energies are measured relative to the top of the valence band, and $E_g = 1.544$ eV.

Defects	E_1 (eV)	E_2 (eV)
$V_{\rm Ga}^{+}$	-0.055	
$V_{\rm Ga}^{0}$	0.035	
$V_{\rm Ga}^{-}$	-0.011	
$V_{\rm Ga}^{2-}$	0.011	0.078
$V_{\rm Ga}^{3-}$	0.034	
$V_{\rm As}^{+}$	1.429	
$V_{\rm As}^{0}$	0.746	1.55
$V_{\rm As}^{-}$	0.735	1.531
$V_{\rm As}^{2-}$	1.059	1.607
${\rm Ga}_{\rm As}^{2+}$	0.134	
${\rm Ga}_{\rm As}^{+}$	0.220	0.570
${\rm Ga}_{\rm As}^{0}$	0.232	
${\rm Ga}_{\rm As}^{-}$	0.285	0.664
${\rm Ga}_{\rm As}^{2-}$	0.300	
${\rm As}_{\rm Ga}^{2+}$	-0.026	
${\rm As}_{\rm Ga}^{+}$	0.517	
${\rm As}_{\rm Ga}^{0}$	0.490	
${\rm As}_{\rm Ga}^{-}$	0.491	1.590

For a given family of defects, i.e., at fixed atomic concentrations, the contribution of atomic chemical potentials in Eq. (2.3) is a constant independent of charge, which can therefore be ignored; only the electronic chemical potential needs to be considered. When comparing defects belonging to different families, however, as will be done in Sec. V, it is necessary to take into account both atomic and electronic chemical contributions.

III. VACANCIES

In the III-V compound semiconductors, where bonding is partly ionic, the anion is more electronegative than the cation. Therefore the creation of a vacancy at an anion site is expected to perturb the system more than at a cation site. Since neutral vacancies in Si lead to levels in the middle of the band gap,[39] it is expected that anion vacancies will lie in the upper half of the gap, i.e., near the conduction-band minimum (CBM), while cation vacancies will lie in the lower half, i.e., near the valence-band maximum (VBM); this has indeed been verified on the basis of theoretical models.[16,20,40,41]

A. Ga vacancies

We start our discussion with Ga vacancies in different states of charge. For tetragonally distorted configurations, it is convenient to describe the relaxation of the neighbors of a given defect in terms of three displacement components:[20,41] the "breathing" mode, which gives the radial relaxation (inwards or outwards) of an ion, and two "pairing" modes, which measure the lateral displacements of the ions (i.e., perpendicular to the breathing mode). The average breathing-mode displacement provides information about OV changes during the relaxation process, whereas the pairing modes describe deviations from the tetrahedral symmetry. Our results for the relaxation of Ga vacancies (as well as other defects to be discussed below) are summarized in Table II. The pairing-mode displacements are negligible here — the tetrahedral symmetry is conserved — and we therefore only give the breathing-mode displacements, as well as the corresponding open volume changes.

Irrespective of their state of charge, we find all Ga vacancies to relax inwards, by an amount which is virtually constant (0.32 ± 0.03 Å, i.e., about 13% of the bulk bond distance, 2.45 Å); correspondingly, the open volume decreases by about 34%. These results are consistent with positron lifetime measurements,[2,5] which find a single value for the lifetime when Ga vacancies alone are present; in view of the sensitivity of the lifetime of the positron to the OV, therefore, it must also be concluded from the measurements that the OV of a Ga vacancy is independent of its state of charge.

Our results for the ionic relaxation are consistent with the first-principles calculations of Laasonen *et al.*[20] who observe no trend in the dependence of the displacements on the state of charge, even though the amplitudes of relaxation are smaller (2.9–3.9 % of the bond length). However, we find that the defect-induced states lie close to the valence-band maximum (within ~0.1 eV — see Table I), as expected, whereas Laasonen *et al.* find the localized states to lie at 0.56–0.62 eV above the VBM, that is, close to the CBM for LDA calculations but near the middle of the experimental band gap.

The variation with electron chemical potential of the formation energy of a defect in various states of charge provides information about its ionization levels. For Ga vacancies, Fig. 1 shows the formation energies obtained from Eq. (2.3) with μ_e in the range 0–0.12 eV, i.e., near the VBM (in principle, $0 \leq \mu_e \leq E_g$, but no changes occur beyond the window considered in Fig. 1). Evidently, our model predicts the existence, for this family of vacancies, of a "negative-U" effect, that is, an effective correlation energy between electrons which is negative.[42] Indeed, the ground state of the defect is singly positive for $\mu_e \leq 0.035$ eV, singly negative for $0.035 \leq \mu_e \leq 0.078$ eV, and triply negative for $\mu_e \geq 0.078$ eV, so that we have the $(+/-)$ ionization level at 0.035 eV and $(-/3-)$ at 0.078 eV. The energy difference between these ionization levels is very small (0.043 eV), close to the limit of accuracy of our model ($\sim$ 0.02 eV — see Sec. II), and should therefore be taken with caution (even though we expect cancellation of systematic and model errors in calculating such energy differences — see Refs. 17 and 43).

Our observation of a negative-U effect is not consistent with other model calculations, but the theoretical situation is not clear; unfortunately, to our knowledge, no experimental data are available that could resolve the issue. Thus, using a spin-unrestricted density functional theory and the linear muffin-tin-orbital Green's function method *without* lattice relaxation, applying a "scissor operator" to force (by a rigid shift of the CBM) the energy gap to its experimental value, Puska[17] finds $(0/-)$, $(-/2-)$, and $(2-/3-)$ ionization levels at 0.11, 0.22, and 0.33 eV, respectively. For the same levels, using a similar approach, Baraff and Schlüter[12] who also ignore lattice relaxation, find 0.2, 0.5, and 0.7 eV. Also using the LDA, but with a self-consistent pseudopotential method for the ion cores, ignoring lattice relaxation, Jansen and Sankey[18] find the three ionization levels to lie within 0.5 eV of the VBM (their estimate of E_g is 1.2 eV). Zhang and Northrup,[19] finally, using the LDA and a 32-atom supercell, considering only breathing-mode relaxation (probably a reasonable assumption, in the light of our own calculations), find all ionization levels to be clustered in the range 0.19–0.32 eV. Thus relaxation, while it may not be sufficient to cause a negative U, apparently leads to clustering of

TABLE II. Nearest-neighbor breathing-mode displacements and local volume changes for the different defects considered in the present work. The average relaxations are given both in Å and relative to the bond distance of bulk GaAs (2.45 Å). + and − refer to outward and inward relaxation, respectively. $\Delta V = V - V_0$ is the change in volume of the defect (i.e., the volume of the tetrahedron formed by the four nearest neighbors) resulting from relaxation.

Defect	Breathing (Å)				Average (Å)	Average (%)	$\Delta V/V_0$ (%)
	1	2	3	4			
$V_{\rm Ga}^{+}$	-0.31	-0.35	-0.31	-0.31	-0.32	-13.1	-34.3
$V_{\rm Ga}^{0}$	-0.33	-0.33	-0.31	-0.30	-0.32	-13.0	-34.1
$V_{\rm Ga}^{-}$	-0.32	-0.32	-0.32	-0.29	-0.32	-12.9	-33.9
$V_{\rm Ga}^{2-}$	-0.32	-0.32	-0.32	-0.30	-0.31	-12.8	-33.7
$V_{\rm Ga}^{3-}$	-0.31	-0.31	-0.31	-0.31	-0.31	-12.8	-33.7
$V_{\rm As}^{+}$	0.38	0.38	0.38	0.38	0.38	15.5	54.0
$V_{\rm As}^{0}$	0.44	0.44	0.44	-0.49	0.21	8.5	24.2
$V_{\rm As}^{-}$	0.39	0.39	0.39	-0.50	0.17	6.8	18.9
$V_{\rm As}^{2-}$	0.45	-0.42	0.45	-0.42	0.02	0.8	-3.3
${\rm Ga}_{\rm As}^{2+}$	0.49	0.49	0.21	0.21	0.35	14.4	50.0
${\rm Ga}_{\rm As}^{+}$	0.48	0.17	0.13	0.13	0.23	9.2	30.0
${\rm Ga}_{\rm As}^{0}$	0.48	0.07	0.07	0.07	0.17	7.0	22.2
${\rm Ga}_{\rm As}^{-}$	0.11	0.02	0.02	0.02	0.04	1.8	5.5
${\rm Ga}_{\rm As}^{2-}$	-0.01	-0.01	-0.01	-0.01	-0.01	-0.3	-1.0
${\rm As}_{\rm Ga}^{2+}$	0.06	0.06	0.06	0.06	0.06	2.5	7.6
${\rm As}_{\rm Ga}^{+}$	0.06	0.06	0.06	0.06	0.06	2.4	7.5
${\rm As}_{\rm Ga}^{0}$	0.06	0.06	0.06	0.06	0.06	2.4	7.5
${\rm As}_{\rm Ga}^{-}$	0.06	0.06	0.06	0.06	0.06	2.5	7.8

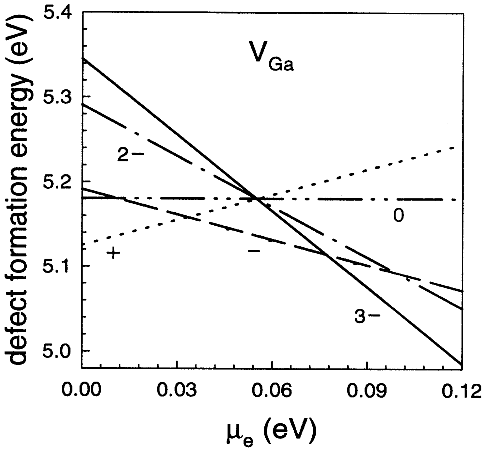

FIG. 1. Defect formation energies vs electron chemical potential for the Ga vacancies in different charge states, as indicated. Here, we have set $\Delta\mu_{\mathrm{Ga}} = -0.85$ eV.

the ionization levels near the VBM.

From the above results, including our own, we conclude that Ga vacancies are preferentially negatively charged (predominantly 3−) for most values of the electron chemical potential, and that ionization levels tend to lie in the lower half of the experimental band gap, i.e., near the VBM. Consistent with this, there is experimental evidence that self-diffusion in GaAs occurs via the diffusion of V_{Ga}^{3-} defects.[44] The existence of a negative U, predicted by our calculations, however, remains to be assessed in detail: Our model may not be accurate enough to provide an unambiguous answer. On the other hand, it is not clear, in LDA calculations, what the effect of a rigid scissor shift is on detailed energy values,[17] and more specifically on the ionization levels.

B. As vacancies

We now turn to As vacancies. Unlike Ga, the relaxation vectors, indicated in Table II for the breathing modes and in Table III for the pairing modes, depend sensitively on the state of charge of the defect; this is particularly evident for the breathing modes and OV changes in Table II. We note that the pairing-mode displacements are in all cases small (≤ 0.03 Å), and therefore have little effect on OV changes.

Breathing-mode displacements, in all cases but V_{As}^{+}, break the local tetrahedral symmetry, in that some neighbors relax inwards and some relax outwards. As indicated in Table II, the OV decreases upon adding electrons and actually changes sign (from outwards to inwards) on going from the − to the 2− state. This behavior was also observed in GaAs by Laasonen *et al.*[20] except that, in their case, the outwards/inwards transition was found to take place on passing from the neutral to the single-negative state. We therefore expect, in view of this, the positron lifetime to be longest for the V_{As}^{+} vacancy (largest volume) and shortest for the V_{As}^{2-} (smallest volume).

TABLE III. Nearest-neighbor pairing-mode displacements for As vacancies and Ga antisites.

Defect	Pairing 1 (Å)				Pairing 2 (Å)			
	1	2	3	4	1	2	3	4
V_{As}^{+}	0	0	0	0	0	0	0	0
V_{As}^{0}	-0.01	-0.01	0.03	0	0.02	0.02	0	0
V_{As}^{-}	-0.01	-0.01	0.02	0	0	0	0	0
V_{As}^{2-}	0.01	-0.01	0.01	-0.01	-0.01	0.01	-0.01	0.01
$\mathrm{Ga}_{\mathrm{As}}^{2+}$	-0.02	-0.02	-0.21	-0.21	0	0	0	0
$\mathrm{Ga}_{\mathrm{As}}^{+}$	0.03	-0.01	-0.12	-0.12	0	0	-0.03	0.03
$\mathrm{Ga}_{\mathrm{As}}^{0}$	0	0.08	-0.04	-0.04	0	0	-0.06	0.06
$\mathrm{Ga}_{\mathrm{As}}^{-}$	0	0.05	-0.03	-0.03	0	0	-0.05	0.05
$\mathrm{Ga}_{\mathrm{As}}^{2-}$	0	0	0	0	0	0	0	0

The lifetimes of positive vacancies (and therefore their OV's) have not been measured using positron annihilation experiments, because of the strong Coulomb repulsion of like charges which cause the trapping rates to approach zero.[5] However, the positron lifetime has been found[2] to decrease from 295 ps to 258 ps when the charge of the As vacancy changes from neutral to singly negative (the positron lifetime in perfect GaAs is, in comparison, 230 ps). On the basis of theoretical calculations using free-atom densities with electron-positron correlation depending on the local electron density,[45,46] it has been found that an 8% breathing-mode relaxation is needed in order to explain the positron lifetime of 295 ps observed for the neutral As vacancy. This agrees very well with our observation of a radial relaxation by 8.5% (cf. Table II), whereas Laasonen *et al.* find only 2%. Mäkinen and Puska,[46] likewise, estimate that a 5–10 % decrease of the breathing-mode relaxation can explain the 30 ps change in positron lifetime observed when the As vacancy ionizes from neutral to negative. While the trend we observe — decrease of the OV upon adding electrons — is consistent with this, the change in radial relaxation, in the case $V_{\mathrm{As}}^{0} \rightarrow V_{\mathrm{As}}^{-}$ about 1.7%, is probably a little low to explain the measured 30 ps difference in lifetime. Laasonen *et al.*, on the other hand, find an 18% change, which is perhaps a little on the high side.[20]

The dependence on the electron chemical potential (close to the CBM) of the formation energies of the As vacancies is displayed in Fig. 2; a behavior quite different from that of Ga vacancies is observed. In particular, we see no negative-U effect here. Measuring the energies relative to the CBM, we find the (+/0) and (0/−) ionization levels at −0.13 and −0.002 eV, respectively. Our values are in very good agreement with the values deduced from positron lifetime measurements[2–4,16] (after considerable efforts in properly identifying the ionization levels), namely, −0.14 and −0.03 eV. In fact, the present calculations constitute the first theoretical confirmation (to our knowledge) of the measured ionization levels of this defect. Puska,[17] for instance, found ionization levels at −0.32, −0.22, and −0.13 eV for (+/0), (0/−), and

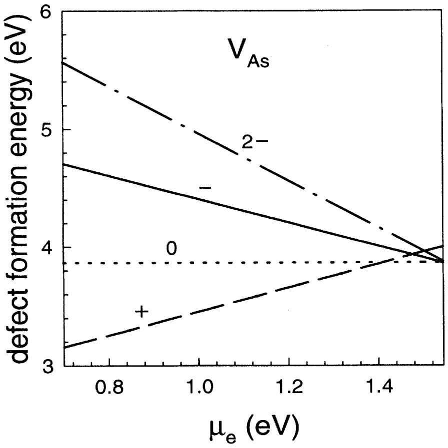

FIG. 2. Same as Fig. 1, but for As vacancies.

(−/2−), respectively. Baraff and Schlüter[12] found a single ionization level, close to the VBM, which they assigned to the (2+/+) transition. Zhang and Northrup[19] observed no ionization but, rather, found $V_{\rm As}^{+}$ to be the lowest energy state for all values of the electron chemical potential, i.e., throughout the gap. Jansen and Sankey,[18] finally, using the LDA, found two ionization levels, *above* the CBM from their calculation, but nevertheless below the experimental CBM; these are the (+/0) transition at −0.30 eV and the (0/−) at −0.20 eV, where the energies are given relative to the top of the experimental band gap.

IV. ANTISITES

Antisites, like vacancies, are fundamental intrinsic defects in compound semiconductors and are more likely to occur when the differences in size and electronegativity between cation and anion are small. Thus they are more likely to be found in GaAs than in GaP and InP. Defects such as antisites in GaAs that introduce deep electronic states with ionization energies of the order of the band gap are considered to be a crucial factor limiting semiconductor device performance and reliability.[47] Later, we will show that antisites are indeed prevalent point defects in GaAs.

A. Ga antisites

We have studied Ga antisites $\mathrm{Ga_{As}}$ from the doubly positive to the doubly negative charge state, as indicated in Table I. Our calculation starts, in each case, with a Ga atom on an As lattice site in the perfect zinc-blende structure, which we then allow to relax fully. The calculated breathing and pairing modes of the nearest neighbors are listed in Tables II and III.

Just like As vacancies, the Ga antisite undergoes large relaxation depending on its charge. The neutral Ga antisite has two electrons less than bulk GaAs (an As with five valence e^- is replaced by a Ga with three e^-), so that adding electrons to the system brings it closer to the normal bulk situation. Indeed, as reported in Tables II and III, almost no relaxation occurs for the doubly negative antisite $\mathrm{Ga_{As}^{2-}}$; in fact, the pairing-mode displacements vanish completely here. It turns out that additional electrons lead to levels in the conduction band (unlike As antisites), and we therefore expect little relaxation for defects in a large negative charge state; we have verified that this was indeed the case. In the opposite situation, however, i.e., when taking electrons out of the system, the perturbation to the system is more important, and leads to a sizable relaxation of the nearest neighbors, as observed here.

For the singly negative antisite $\mathrm{Ga_{As}^{-}}$, there is a small (<2%) outwards breathing-mode displacement, and similar pairing-mode relaxations of the nearest neighbors. In fact, the antisite itself is displaced slightly from its ideal lattice position, by about 0.1 Å in the $\langle 11\bar{1}\rangle$ direction. The distance between the antisite and one of its Ga neighbors, which we label "$\mathrm{Ga_1}$" following Zhang and Chadi[15] [see Fig. 3(a)], is 2.65 Å, a little bit longer than 2.45 Å, the nearest-neighbor distance in ideal zinc-blende GaAs. The distance between the Ga antisite and the three other Ga neighbors, which relax very little, is 2.44 Å. This atomic structure near $\mathrm{Ga_{As}^{-}}$ is very similar to the results of Zhang and Chadi[15] who studied the problem using the *ab initio* self-consistent pseudopotential method in the local density functional approximation.

For the neutral Ga antisite, depicted in Fig. 3(b), we find the defective atom to move 0.4 Å away from the ideal bulk site along the $\langle 11\bar{1}\rangle$ direction; the $\mathrm{Ga_1}$ neighbor also moves away, but in the opposite direction, by 0.48 Å. This leads to a "broken-bond" configuration with a relaxed $\mathrm{Ga_{As}^{0}}$-$\mathrm{Ga_1}$ distance of 3.32 Å, in perfect agreement with Zhang and Chadi's calculation.[15] Both the antisite and $\mathrm{Ga_1}$ form quasiplanar configurations with their nearest neighbors, lying respectively 0.37 and 0.33 Å away from the planes (compared with 0.82 Å for the perfect zinc-blende structure). The average bond lengths and angles between $\mathrm{Ga_{As}^{0}}$ and its three Ga neighbors are 2.42 Å and 117.8°, while between $\mathrm{Ga_1}$ and its three As neighbors

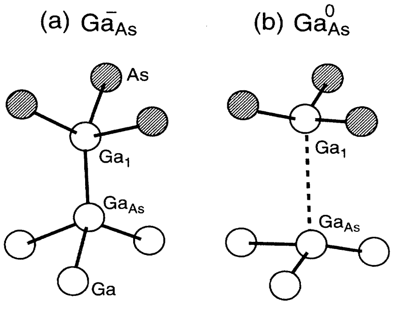

FIG. 3. Local relaxed atomic configuration for (a) the negative and (b) the neutral Ga antisite.

we find 2.41 Å and 118.4°, also in excellent accord with the results of Zhang and Chadi.[15] Positively charged Ga antisites, finally, show similar relaxations, as manifest for instance by large OV changes — cf. Table II; the $\mathrm{Ga_{As}}$-$\mathrm{Ga_I}$ distance is found to be 3.33 and 3.29 Å for the + and 2+ states, respectively.

We note, from Tables II and III, that two families of defects, the As vacancies and the Ga antisites, exhibit a strong dependence of relaxation on the state of charge (As antisites exhibit relatively small relaxations, as discussed next). Evidently, Ga-rich material is perturbed more than As-rich material. It is not clear what this effect is due to, but it may be related to the (small but nevertheless finite) size difference between Ga and As, as well as to the transfer of charge between the two in the presence of defects.

We have calculated the defect formation energies of the Ga antisites using Eq. (2.3); the results (as a function of the electron chemical potential) are displayed in Fig. 4. Again, here, we observe a negative-U effect: ionization of the defect occurs at 0.706 eV for the (2+/0) process, and at 0.896 eV for (0/2−). The (0/2−) ionization was also observed by Zhang and Chadi,[15] though at a value of μ_e closer to the VBM, 0.17 eV, as well as by Zhang and Northrup[19,35] at 0.38 eV. It should be said that, in the latter two calculations, only breathing-mode relaxation was allowed, whereas full relaxation was permitted in our case. Relaxation is believed to be an important contribution in the detailed balance of energy that may or may not give rise to a negative-U effect.[39] In fact, in a calculation of this defect which neglected relaxation, Baraff and Schlüter[12] found ionization levels at 0.3 and 0.62 eV for (0/−) and (−/2−), respectively, i.e., no negative-U effect, while Puska[17] found 0.11 and 0.28 eV.

Experimentally,[48,49] a negative-U effect has not been observed; the reported ionization levels carry large error bars, however, varying in the range 0.077 to 0.4 eV for the (0/−) transition, and 0.23 to 0.7 eV for the (−/2−) transition. It would be of considerable interest that new, detailed, and careful measurements be carried out in order to resolve the discrepancy between theoretical calculations and previous experiments, i.e., to determine whether $\mathrm{Ga_{As}^-}$ is a metastable state or not.

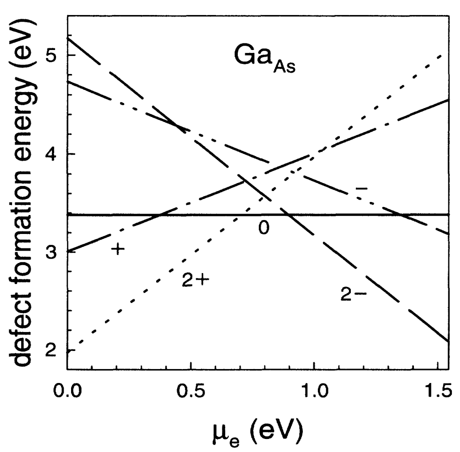

FIG. 4. Same as Fig. 1, but for Ga antisites.

B. As antisites

Lastly, we have studied the $\mathrm{As_{Ga}}$ family of antisites. As reported in Table II, As antisites undergo relatively small relaxations, which, as is the case with Ga vacancies, depend very little on the state of charge. The average breathing displacement amounts to about 2.5% of the bulk GaAs nearest-neighbor distance, and the pairing modes vanish, i.e., the tetrahedral symmetry is preserved in all cases considered here.

Consistent with our results, first-principles calculations find,[10,11,50] for the neutral As antisite, a purely radial (outwards) relaxation, in the range 1–8 %. Likewise, scanning tunneling microscopy (STM) measurements, which can probe bulklike defects when surfaces do not reconstruct [in this case the (110)],[22] find the local tetrahedral symmetry to be preserved. Tunneling spectroscopy, in addition, reveals that the defect states lie in the gap at an energy 0.5 eV above the VBM,[22] in excellent accord with our value of 0.49 eV for the neutral As antisite (Table I), as well as with Dabrowski and Scheffler's 0.6 eV.[10]

In a way similar to $\mathrm{Ga_{As}}$, we find a negative-U effect for the (2+/0) ionization level at 0.517 eV above the VBM, as demonstrated in Fig. 5. This negative-U ionization is consistent with the value of 0.8 eV calculated by Zhang and Northrup,[19,35] whereas Puska[17] finds no negative U but, rather, a (2+/+) transition at 0.88 eV and a (+/0) transition at 1.07 eV. For the same transitions, Baraff and Schlüter[12] find 1.25 eV and 1.5 eV, respectively, while experimentally Weber *et al.*[9] observe 0.52 eV and 0.75 eV.

It is generally understood that the As antisite is responsible for the $EL2$ level;[10–14,51] our calculations support this view. More specifically, it is believed that the $EL2$ defect is neutral, lies at midgap, and possesses tetrahedral symmetry; all three properties are accounted for by our TB model.

V. DEFECT FORMATION ENERGIES

Compound semiconductors can be grown under conditions of controlled nonstoichiometry. For example, a

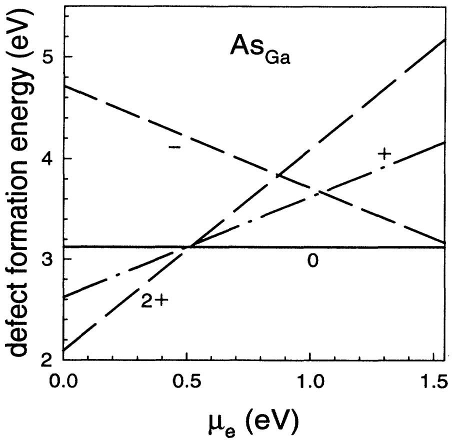

FIG. 5. Same as Fig. 1, but for As antisites.

GaAs crystal containing an excess of As will accommodate this excess by increasing its concentration of defects: whether these are As interstitials, As antisites, Ga vacancies, or a combination of these, is determined by thermodynamic considerations involving the total energies of the defects. It is therefore important to have detailed knowledge of the energetics of defects, and to compare them with one another in order to determine the thermodynamically most favorable one under nonstoichiometric conditions. For this purpose, it is necessary to take into account, in the calculation of the defect formation energies, the contributions of both electron and atomic chemical potentials, as discussed in Sec. II.

The value of the electron chemical potential lies in the range $0 \le \mu_e \le E_g$ (=1.544 eV), measured from the top of the valence band. In the following, results are presented for three representative values of μ_e, namely, at the VBM, at midgap ($E_g/2$), and at the CBM. The range of values for the atomic chemical potentials can be determined by demanding that the defect formation energies be positive in the thermodynamic limit. An additional constraint is provided by calculating the total energy of bulk Ga, which yields an upper limit for $\mu_{\rm Ga}$. Combining those two conditions, we obtain (approximately) -5.0 eV $\le \mu_{\rm Ga} \le -3.5$ eV, i.e., in the language of Eq. (2.3), -1.5 eV $\le \Delta\mu_{\rm Ga} \le 0$, where the lower and upper limits correspond to As-rich and Ga-rich conditions, respectively. Strictly speaking, we have (from experiment) $-\Delta H = -0.74$ eV $\le \Delta\mu_{\rm Ga} \le 0$, but because of uncertainties in the TB description of the bulk Ga phase the upper limit of the $\Delta\mu_{\rm Ga}$ range is not known precisely.

Figure 6 shows, for each of the three values of μ_e considered, the defects of lowest energy as a function of $\Delta\mu_{\rm Ga}$. At both the VBM and midgap, the As antisite is the most favorable defect in the As-rich limit, while the Ga antisite is the one preferred in the Ga-rich limit. In the middle of the $\Delta\mu_{\rm Ga}$ range, however, the vacancies $V_{\rm As}^{+}$ and $V_{\rm Ga}^{3-}$ take over at midgap, though in only a narrow window of values. At the CBM, now, $V_{\rm Ga}^{3-}$ dominates in As-rich conditions, while the ${\rm Ga}_{\rm As}^{2-}$ is favored in the Ga-rich limit. Thus, overall and by large, antisites have lowest energies, and we therefore expect these defects to be much more prevalent than vacancies in GaAs. This, again, is consistent with the current interpretation of the *EL*2 defect, frequently observed in real laboratory samples, being an As antisite. It should be noted that in the Ga-rich limit interstitials have been shown to play an important role;[19] a study of interstitials within the present framework is, however, beyond the scope of our study.

We can use Fig. 6 to understand the results of a positron annihilation study of *n*-type GaAs,[52] which found the lifetime of unidentified monovacancies to be rather insensitive to the value of the electron chemical potential. On the basis of our study, we suggest that the defect in question is in fact a Ga vacancy, whose open volume is found to be independent of its charge state. Thus As is in excess in the sample. In the As-rich limit, near the CBM (since the sample is *n*-type), and for small values of the formation energy (0.57 eV in the present case), we find that the Ga vacancy is in a triply negative charge state. We therefore conclude that the defect observed in Ref. 52 is the ${\rm Ga}^{3-}$ vacancy.

VI. SUMMARY AND CONCLUDING REMARKS

In this paper, we have presented a detailed tight-binding molecular-dynamics study of the effect of defects (vacancies and antisites) in different states of charge on the electronic and structural properties of GaAs. Relaxation was fully included in our model, and for each defect we calculated the local atomic structure, the volume change upon relaxing, the formation energy (including chemical potential contributions), and the ionization levels. Overall, the model is found to provide good agreement with first-principles calculations, as well as experimental data when available.

Our results can be summarized as follows.

(i) Ga vacancies relax by an amount which is independent of the state of charge, about 34% inwards in volume, consistent with positron lifetime measurements. They lead to states in the gap that lie close to the valence-band maximum. Ga vacancies are found, also, to exhibit a negative-*U* effect, and to assume a triply negative charge state for most values of the electron chemical potential.

(ii) The relaxation of As vacancies, on the contrary, depends sensitively on the state of charge; from a large

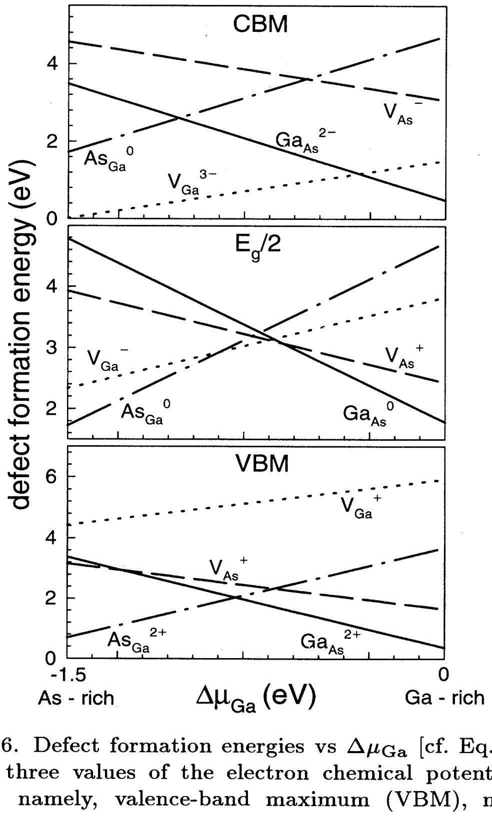

FIG. 6. Defect formation energies vs $\Delta\mu_{\rm Ga}$ [cf. Eq. (2.3)] for the three values of the electron chemical potential indicated, namely, valence-band maximum (VBM), midgap ($E_g/2$), and conduction-band minimum (CBM). The lower and upper limits of the $\Delta\mu_{\rm Ga}$ range correspond to As- and Ga-rich regions, respectively.

outwards volume relaxation of 54% in the $+$ state, relaxation changes sign upon going from the $-$ to the $2-$ state. The model predicts correctly the existence of two ionization levels for this defect just below the conduction-band minimum.

(iii) Likewise, Ga antisites exhibit large relaxations. In fact, in the neutral state, relaxation is so large that it leads to a "broken-bond" configuration, in excellent accord with the first-principles calculations of Zhang and Chadi.[15] This system also exhibits a negative-U effect, for values of the electron chemical potential near midgap. It would be of considerable interest that detailed measurements be carried out in order to verify this prediction of our model.

(iv) For As antisites, we find only a weak relaxation, independent of the charge, in agreement with first-principles studies and scanning tunneling microscopy measurements. A negative-U ionization level is observed at 0.52 eV above the valence-band maximum. Our model predicts the neutral state of the defect to be the ground state for values of the electron chemical potential near and above midgap, which supports the view that the $EL2$ defect is a neutral As antisite.

(v) Upon comparing the formation energies of the various defects, we find that, for all values of the atomic chemical potentials, antisites are more likely to occur than vacancies — $\mathrm{As_{Ga}}$ in As-rich conditions and $\mathrm{Ga_{As}}$ in Ga-rich conditions.

The tight-binding molecular-dynamics approach used here, which was developed using bulk properties alone, is evidently able to account for the properties of systems in configurations of reduced symmetry. We have considered here the case of point defects; we have also examined the relaxation of surfaces, and obtained excellent agreement with first-principles calculations.[53] We conclude that this model represents a good alternative, for some problems at least, to detailed quantum-mechanical calculations.

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