Structural properties and energetics of oxygen impurities in GaAs

Walter Orellana

Departamento de Física, ICEx, Universidade Federal de Minas Gerais, CP 702, 30123-970, Belo Horizonte MG, Brazil

A. C. Ferraz

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo SP, Brazil

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We investigate the structural properties, formation energies, and electronic structure of oxygen impurities in GaAs using first-principles total-energy calculations. Five charge states of oxygen occupying an arsenic site (O_{As}) and various interstitial sites (O_i) were considered. For the O_{As} defect in negative charge states we find off-center configurations with C_{2v} symmetry as reported experimentally. Our results for the formation energies reveal a negative-U behavior for the O_{As} defect, in which the paramagnetic $2-$ charge states is never stable. For the O_i defect, we find three equilibrium configurations for the O atom, which are present in all the charge states investigated. The stable configuration for the neutral defect shows the O atom between an As-Ga pair forming the As-O-Ga structure. However, for the negative charge states, the stable configuration shows the O atom exactly at the tetrahedral interstitial site, bonding with four gallium first neighbors. Further, we find that the $1-$ charge state is never stable, suggesting that the interstitial defect also exhibits a negative-U behavior. Based on our results, we suggest that the A, B', and B bands of the local-vibrational-mode absorption spectrum of oxygen in GaAs are due to the off-center O_{As} defect. Also we show that this spectrum cannot be associated with an interstitial-oxygen configuration as previously proposed.

I. INTRODUCTION

Oxygen in GaAs has been the subject of intense research for decades. The interest in this impurity was initially motivated by the semi-insulating behavior related to oxygen-doped GaAs and more recently by its incorporation as an important contaminant during growth process. Although the experimental characterization of oxygen in GaAs appears to be well established, recent theoretical studies have suggested new interpretations for the experimental data.

Local vibrational mode (LVM) spectroscopy[1–4] has revealed the presence of two oxygen-related defects in GaAs: interstitial (O_i) and substitutional at the arsenic site (O_{As}). For the substitutional defect, the vibrational mode measurements suggest that the O atom moves off-center from the arsenic site toward two neighboring Ga atoms, forming the Ga-O-Ga structure. A set of three triplets of the LVM absorption lines, located at around 730.7, 714.2, and 714.9 cm^{-1}, have been reported so far.[2] These triplets, labeled as A, B', and B, respectively, have been attributed to the vibrational frequencies of oxygen bonding with two gallium isotopes (^{69}Ga and ^{71}Ga), in three different charge states. Detailed experiments also show that the middle charge state, associated with the B' band, is unstable, revealing a negative-U behavior for this center.[5] Furthermore, recent optically detected electron-paramagnetic-resonance studies[6,7] have identified the unstable state as paramagnetic, suggesting that it would be the neutral charge state. On the other hand, LVM measurements associated with the interstitial defect[4] suggest that the O atom breaks the bond between an As-Ga pair, bonding with each atom in an As-O-Ga bridge configuration. Two sharp lines of the LVM spectrum located at around 845 cm^{-1} are associated with the stretching mode the As-O-Ga structure.

There exist a few theoretical studies related to the oxygen impurity in GaAs. The O_{As} defect has been studied by Jones and Öberg,[8] using a local-density-functional cluster method. In this work, they report an off-center displacement of the O atom along the [001] direction from $1-$ to $3-$ charge states, indicating a negative-U behavior. Based on these results, they suggest that the off-center substitutional oxygen, usually termed as V_{As}-O, would be similar to the A center in silicon.[9] More recent first-principles calculations by Mattila and Nieminen,[10] employing the plane-wave pseudopotential method with a 32-atom supercell, have reported the same off-center displacement for substitutional oxygen as found by Jones and Öberg. The new findings in this work are two unstable charge states, the neutral and doubly negative, suggesting two negative-U behaviors for the O_{As} defect. For the O_i defect they found an As-O-Ga structure, in agreement with experimental results, which would only exists in neutral charge state. However, very recent *ab initio* calculations by Taguchi and Kageshima,[11] using the same plane-wave method and supercell size employed by Mattila and Nieminen, have reported different results for both oxygen centers. They conclude that an interstitial oxygen configuration, forming the Ga-O-Ga structure, would be responsible for the negative-U behavior experimentally observed. They also find the off-center configuration for the substitutional oxygen in negative charge states, but at variance with previous theoretical results, their calculations suggest that the V_{As}-O structure is stable from the $1-$ to the $3-$ charge states, with no unstable charge state or negative-U system being observed.

The controversy on the nature of the negative-U behavior and the atomic structure of the oxygen center in GaAs, among recent theoretical calculations, shows that various aspects relate to this defect are not fully understood. In the present work, we perform exhaustive calculations on the

equilibrium geometry, formation energy, and electronic structure for the substitutional and interstitial oxygen impurities in GaAs, employing first-principles total-energy calculations. Our results for the O_{As} defect in positive and neutral charge states show an on-site configuration with T_d symmetry, and for negative charge states an off-center configuration with C_{2v} symmetry. In addition, the singly negative defect exhibits two slightly degenerate equilibrium configurations, with T_d and C_{2v} symmetries. Our results for the formation energies reveal that the paramagnetic $2-$ charge state is never stable, suggesting a negative-U behavior for the off-center O_{As} defect. For the interstitial defect we find three equilibrium positions for the O atom in the lattice. In the neutral charge state we find a stable configuration with oxygen bonding with both As and Ga atoms, forming an As-O-Ga bridge structure. However, for the negative charge states we find a stable configuration with oxygen located at the tetrahedral interstitial site, bonding with four gallium first neighbors. Further, we find that the singly negative charge state is never stable, suggesting that the interstitial defect also forms a negative-U system.

II. THEORETICAL METHODS

Our calculations are based on the density-functional theory[12] (DFT) in the local-density approximation (LDA). We use the form for the exchange-correlation functional given by Ceperley and Alder,[13] as parametrized by Perdew and Zunger.[14] The Kohn-Sham equations are solved employing the molecular dynamics scheme suggested by Car and Parrinello,[15] together with the norm-conserving soft Troullier-Martins pseudopotential.[16] We have treated the Ga $3d$ electrons by the nonlinear core correction[17] throughout this work. We use the supercell approach with a fully relaxed 32-atom supercell. The wave functions are expanded into plane waves up to a kinetic energy cutoff of 60 Ry. The convergence of total energy with respect to the plane-wave basis set was checked considering higher cutoff energy (80 Ry). The difference with respect to the 60-Ry results is found to be 0.18 eV. The Brillouin-zone sampling is performed with two and four special **k** points.[18] Four **k** points were used to describe equilibrium geometries involving off-center distortions and low-symmetry configurations. The difference in total energy between calculations using two and four **k** points is found to be less than 0.05 eV. The structural optimization is performed by calculating the Hellmann-Feynman forces on the ions. The atomic positions are considered relaxed when these forces are less than 0.05 eV/Å. A detailed description of the computational method is given in Ref. 19.

To calculate the formation energies of the impurity systems, we use a widely established method.[20,21] In this method, the parameters are the atomic chemical potentials (μ_{Ga}, μ_{As}, and μ_O) and, for charged systems, the electron chemical potential or Fermi level (μ_e). Thus, the formation energy of the oxygen impurity in GaAs in the charge state q can be written as

$$E_f(q) = E_t(q) - n_{Ga}\mu_{Ga} - n_{As}\mu_{As} - \mu_O + q(\mu_e + E_v), \quad (1)$$

where E_t is the total energy of the impurity system derived from the supercell calculation and n_{Ga} (n_{As}) is the number of

Ga (As) atoms in the supercell. The Fermi level μ_e is measured relative to the top of the valence band E_v. The atomic chemical potentials can vary over a range given by the heat of formation of GaAs, defined as $H_f = E_{Ga(bulk)} + E_{As(bulk)} - E_{GaAs(bulk)}$. We obtain $H_f = 0.61$ eV. Additionally, the atomic chemical potential are constrained by the equilibrium condition $\mu_{Ga} + \mu_{As} = \mu_{GaAs(bulk)}$. Upper bounds for μ_{Ga} and μ_{As} are given by their respective bulk phases, $\mu_{Ga} < \mu_{Ga(bulk)}$ and $\mu_{As} < \mu_{As(bulk)}$. To establish an upper limit for the chemical potential of the oxygen impurity, we consider the formation of gallium oxide (Ga_2O_3). An upper bound for μ_O is then obtained from the relation $2\mu_{Ga} + 3\mu_O = \mu_{Ga_2O_3}$.

For bulk GaAs we find an equilibrium lattice constant $a_0 = 5.607$ Å, and a bulk modulus $B = 0.80$ Mbar,[22] which are in good agreement with the experimental values ($a_0 = 5.653$ Å and $B = 0.77$ Mbar).[23] For the band structure we obtain a direct band gap of 1.30 eV. Bulk arsenic and gallium have been studied previously in detail by *ab initio* calculations.[20,24] We have used the same procedure to find the equilibrium parameters as described in these works, considering a larger cutoff energy of 48 Ry to ensure the total-energy convergence. For the calculation of bulk Ga we use 72 special **k** points[18] in the irreducible part of the Brillouin zone. Our results for the equilibrium lattice constant and internal parameters for the orthorhombic unit cell are $a = 4.432$ Å (4.511 Å), $u = 0.1556$ (0.1525), and $v = 0.0785$ (0.0821), with the experimental values given in parentheses.[26] For the calculation of bulk As we use 48 special **k** points.[18] The equilibrium lattice constant and the internal parameter for the hexagonal unit cell and their respective experimental values are[25] $a = 3.622$ Å (3.759 Å) and $u = 0.2260$ (0.2276). The Ga_2O_3 crystal forms a rhombohedral structure that can be represented by a 10-atom hexagonal unit cell. To calculate its equilibrium structure, we fix the c/a ratio of the hexagonal cell to its experimental value (2.697).[26] We find an equilibrium lattice constant $a = 4.927$ Å, which is within 1% of the experimental value (4.979 Å).

III. RESULTS AND DISCUSSION

A. Substitutional oxygen in GaAs

Our results for oxygen occupying an arsenic site in GaAs, in neutral charge state, show an on-site defect with T_d symmetry with the first-neighbor Ga atoms exhibing a large inward breathing relaxation. The O-Ga bond length is found to be 2.12 Å, about 13% shorter than the As-Ga bond length of bulk GaAs (2.43 Å), while the bond length between the first- and second-neighbor atoms is $\sim$ 2% longer. This relaxation is accompanied by an energy gain of 1.1 eV. According to our LDA calculation, the electronic structure of the O_{As}^0 defect (Fig. 1) shows an electrically active defect with an a_1 singlet state located in the lower part of the band gap occupied by a single electron. Therefore, it suggests that this defect acts as a deep acceptor. Additionally, an empty singlet state is found as a resonance in the bottom of the conduction band. We find that the gap state has an antibonding s-like character where the corresponding bonding state is found hyperdeep in the valence band, about 20 eV below the gap state.
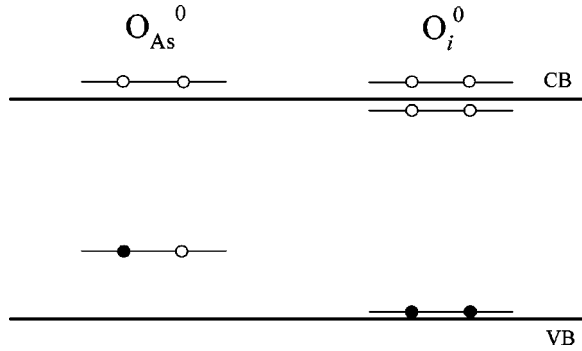
FIG. 1. Schematic representation of one-electron levels in the band gap induced by the oxygen impurity in GaAs in neutral charge state, occupying an arsenic site (O_{As}), and at the stable interstitial site (O_i). The filled dots indicate electrons and the open dots indicate holes.

For the $1-$ charge state, we find two nearly degenerate equilibrium position for the O atom. The stable position is found with oxygen displaced by 0.72 Å from the arsenic site, along the [001] direction, and the metastable position at the arsenic site. We find that the metastable position is 0.09 eV higher in energy than the stable position. The height of the barrier that separates the two equilibrium positions is calculated in 0.2 eV. For the $2-$ and $3-$ charge states we find a V_{As}-O structure, where the O atom moves off-center from the arsenic site along the [001] direction by 0.67 and 0.61 Å, respectively, forming strong Ga-O-Ga bonds as well as a weaker Ga-Ga bond.

In Table I, we summarize the equilibrium geometries for the substitutional oxygen in different charge states. In addition, we include the relaxation energies in order to examine the stability of the defects. These energies are calculated by the difference in total energy between the relaxed and the unrelaxed structures. We find that the positive defect has the lowest relaxation energy (0.78 eV) and the largest O-Ga bond lengths among the systems under study. This because O_{As}^{1+} is an isoelectronic defect with unoccupied dangling bonds. For neutral and singly negative charge states, one and two electrons occupy the antibonding gap state, respectively. The equilibrium geometry of the defect in these charge states show an increase in the relaxation energy and a decrease in the O-Ga bond lengths, suggesting that the O-Ga bonds become stronger with the addition of electrons. This behavior, also observed in previous calculations,[10,11] should not be expected because the antibonding character of the gap state.

TABLE I. Stable configurations of oxygen occupying an arsenic site in GaAs in various charge states. θ is the Ga-O-Ga angle and d is the O-Ga bond length. E_r represents the energy gain due to the atomic relaxation.

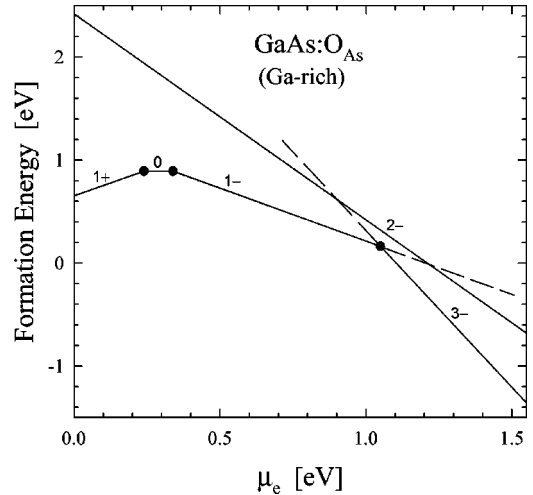| Charge	Symmetry	θ (deg)	d (Å)	E_r (eV)
1+	T_d	109.5	2.14	0.78
0	T_d	109.6	2.12	1.10
1−	C_{2v}	129.5	1.89	1.37
2−	C_{2v}	128.3	1.91	1.66
3−	C_{2v}	126.7	1.92	2.11

FIG. 2. Formation energy as a function of the Fermi level (μ_e) for oxygen occupying an arsenic site in GaAs under a gallium-rich condition, $\mu_{Ga} = \mu_{Ga(bulk)}$. The slopes of the line segments represent the charge states of the systems and the dots indicate the transition states.

We now discuss the energetic of the substitutional defect in GaAs for a Ga-rich condition. Figure 2 shows the formation energies for O_{As} in different charge states as a function of the Fermi level (μ_e). In this figure the slopes of the line segments correspond to different charge states of the systems. Changes in the slopes indicate transition states, which are represented by dots. The range of variation for μ_e is chosen to be the value of the experimental gap of GaAs (1.54 eV).[23] We observe that substitutional oxygen can exists in four charge states $(1+, 0, 1-, 3-)$, where the $2-$ charge state is never stable, showing a negative-U behavior for this defect. From the ionization energies of the $(1-/2-)$ and $(2-/3-)$ transition states we find $U = E^{(1-/2-)} - E^{(2-/3-)} \approx -0.3$ eV. The error bars for the ionization energies are estimated to be about 0.1 eV. In Fig. 2 we observe low formation energies for the off-center configuration in semi-insulating and n-type GaAs (Fermi level in the middle of the gap and close to the bottom of the conduction band, respectively). This is because the empty singlet state, which is resonant in the bottom of the conduction band for the neutral defect, enters into the gap for the negative defects induced by the oxygen distortion. Thus, the V_{As}-O defect can become negatively charged, lowering considerably its formation energy and consequently increasing the likelihood of its occurrence. For p-type GaAs (Fermi level close to the top of the valence band), the on-site substitutional defect can exist in positive charge state. However, the neutral defect is unlikely to occur due to its relatively high formation energy and the narrow range of the Fermi level where it exists.

According to our results, we can assign the A, B', and B bands of the LVM absorption spectrum to the $1-$, $2-$, and $3-$ charge states of the V_{As}-O defect, respectively, as previously proposed by the Mattila and Nieminen calculations.[10] Two arguments support that this charge-state assignment is consistent. The first is the negative-U behavior suggested by our calculations, where the unstable $2-$ charge state corresponds to a paramagnetic state of the defect, in agreement with the experimental observation of the B' band.[7] The sec-
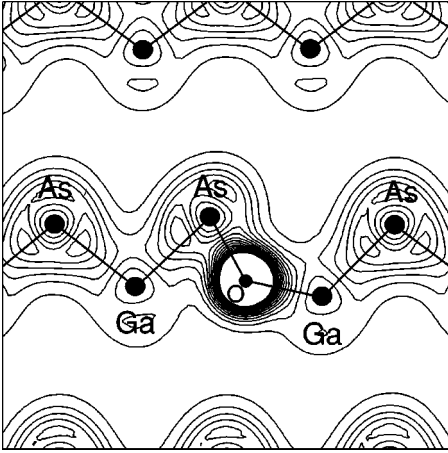
FIG. 3. Total electronic charge density through the (110) plane for the neutral O_i defect in GaAs in its stable configuration, the As-O_i-Ga structure.
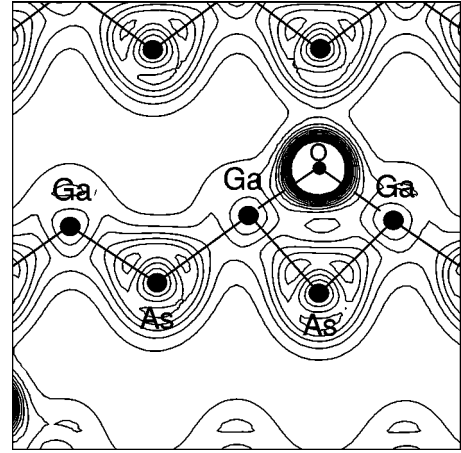

FIG. 4. Total electronic charge density through the (110) plane for the neutral O_i defect in GaAs in the lowest-energy metastable configuration, the Ga_2-O_i-Ga_2 structure.

ond argument is the similarity to the O-Ga bond lengths observed in the V_{As}-O defect for the $2-$ and $3-$ charge states. These bond lengths exhibit variations by about 0.01 Å, suggesting that the corresponding vibrational frequencies might be nearby, which is indeed observed for the B' and B bands. However, recent theoretical calculations by Taguchi and Kageshima have suggested that the $2-$ charge state of the V_{As}-O defect would be stable,[11] but in a very narrow range of the Fermi level. Nevertheless, the imprecision of the calculated ionization energies due to the supercell approach prevent a more accurate prediction for the V_{As}-O negative-U term.

B. Interstitial oxygen in GaAs

To find the minimum energy configuration for the O_i defect in GaAs, we consider various interstitial sites into the lattice as a starting positions for the O atom in our molecular dynamic calculation. These sites are *bonding* (B), Ga-*antibonding* (AB_{Ga}), As-*antibonding* (AB_{As}), Ga-*tetrahedral* (T_{Ga}), and As-*tetrahedral* (T_{As}). Additionally, we consider a site in the middle of two neighboring Ga atoms (C_{Ga}). This procedure is necessary in order to find the stable position for the O atom as well as to identify possible metastable positions, which are frequently found in interstitial defects.

Our results show three equilibrium configurations for the interstitial oxygen in GaAs in neutral charge states. In the first configuration, oxygen breaks the bond between an As-Ga pair forming the As-O_i-Ga structure, as shown in Fig. 3. This equilibrium position is equally obtained from B, AB_{Ga}, AB_{As} and C_{Ga} starting positions. In the second configuration, oxygen is located at the T_{Ga} site, bonding with four Ga atoms (Ga_2-O_i-Ga_2 structure). In Fig. 4 this configuration is shown through the (110) plane. Here we observe strong O-Ga bonds with a substantial inward breathing relaxation of the neighboring Ga atoms, preserving the T_d symmetry. A similar bonding structure is found through the $(1\bar{1}0)$ plane. Finally, in the third equilibrium configuration oxygen is located at the T_{As} site, weakly bonded with four As atoms (As_2-O_i-As_2 structure). In contrast to the second configuration, in this system no significant distortion of the

neighboring As atoms is observed. The As_2-O_i-As_2 structure is the highest in energy with respect to the other two configurations described above in all the charge states investigated. The smallest difference in the total energies between As_2-O_i-As_2 and the following lower-energy structure is found for the neutral charge state. This difference is calculated to be ~ 0.7 eV thus, we will analyze only the two lower-energy configurations.

For the neutral charge state the minimum-energy configuration is the As-O_i-Ga structure. We find Ga-O and O-As bond distances of 1.83 and 1.76 Å, respectively, and a Ga-O-As angle of 131°. The metastable configuration in the neutral charge state is the Ga_2-O_i-Ga_2 structure. In this geometry, the four neighboring Ga atoms relax radially toward the O atom by about 0.3 Å from their ideal positions. We find Ga-O bond distances of 2.13 Å and Ga-O-Ga angles of 109.5°, which are almost the same observed for the O_{As}^0 defect. This configuration is 1.32 eV higher in energy than the minimum-energy configuration.

For the O_i^{1+} defect we find the same stable and metastable structures as found for O_i^0. However, for the negative charge states ($1-$, $2-$, and $3-$) we find the opposite situation, *i.e.*, the stable configuration is now the Ga_2-O_i-Ga_2 structure, while the metastable one is the As-O_i-Ga structure. In Table II we summarize our results for the stable geometries of the O_i defect in their various charge states, also we have calculated the difference in total energy between the two lower-energy configurations. Here we note that in the $1-$ charge state both bonding structures are nearly degenerate, with the Ga_2-O_i-Ga_2 structure being 0.02 eV higher in energy than the As-O_i-Ga structure.

The electronic structure of the stable O_i^0 defect (Fig. 1) shows an electrically inactive defect with two a_1 singlet states into the band gap, one fully occupied close the top of the valence band and the other one empty nearby the bottom of the conduction band. The positions of these energy levels correspond to the stable As-O_i-Ga structure. For the metastable Ga_2-O_i-Ga_2 structure we find the same energy levels and occupancy than the stable one, but with both empty singlet states into the band gap.

TABLE II. Stable configurations of interstitial oxygen in GaAs in various charge states. d_1 and d_2 are the Ga-O and O-As bond lengths, respectively, and θ is the angle between bonds. ΔE_t represents the difference in total energy between the two lower-energy configurations, defined as $\Delta E_t = E_t(\text{Ga}_2\text{-O}_i\text{-Ga}_2) - E_t(\text{As-O}_i\text{-Ga})$. The bond lengths are in Å and the energies in eV.

Charge	Structure	θ (deg)	d_1	d_2	ΔE_t
1+	As-O$_i$-Ga	131.3	1.83	1.75	1.26
0	As-O$_i$-Ga	131.1	1.83	1.76	1.32
1−	Ga$_2$-O$_i$-Ga$_2$	109.5	2.13		−0.02
2−	Ga$_2$-O$_i$-Ga$_2$	109.4	2.12		−1.00
3−	Ga$_2$-O$_i$-Ga$_2$	109.5	2.11		−1.51

Figure 5 shows our results for the formation energy of the interstitial oxygen in GaAs for both bonding structures. We observe that for p-type and semi-insulating GaAs, the neutral As-O$_i$-Ga structure has the lowest formation energy and, therefore, is the energetically most favorable configuration. On the other hand, for n-type GaAs, the Ga$_2$-O$_i$-Ga$_2$ structure in 2− and 3− charge states is the most favorable. However, the singly negative charge state is found energetically unfavorable in both bonding structures. Our calculations suggest that, because of the change in the oxygen stable configuration, the O$_i^0$, O$_i^{1-}$, and O$_i^{2-}$ defects form a negative-U system. The 1− unstable charge state, which corresponds to a paramagnetic state of the interstitial defect, cannot be associated to the B' band of the LVM spectrum because the A, B', and B bands are due to a combination of two gallium isotopes bonding with oxygen. However, the two lower-energy configurations of O$_i$, in neutral and negative charge states, show oxygen bonding with one and four Ga atoms, respectively.

Although our results for the formation energies of the O$_i$ defect show some similarity with those reported by Taguchi and Kageshima, the equilibrium configurations of the O atom exhibit important discrepancies. The main difference resides in the number of Ga atoms bonding with oxygen in the stable
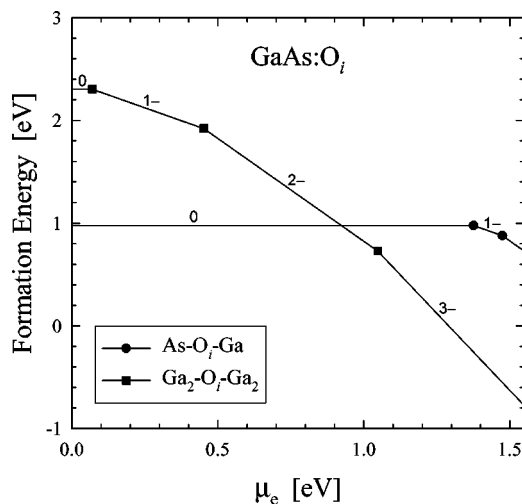

FIG. 5. Formation energy as a function of the Fermi level (μ_e) for the interstitial oxygen in GaAs in their two lower-energy configurations. The slopes of the line segments represent charge states of the systems, and the symbols indicate the transition states.

configuration of neutral and negative defects. For the neutral charge state, Taguchi and Kageshima found a stable configuration with oxygen bonding, almost in line, with two neighboring Ga atoms. In contrast, our results show that the geometry with oxygen located at the middle of two neighboring Ga atoms (our C$_{\text{Ga}}$ starting point) is a non-equilibrium position in all the charge states investigated.

According to our calculations, the stable position of the neutral defect forms the As-O$_i$-Ga structure. This structure is also found by Mattila and Nieminen calculations and agrees with the experimental observation by Schneider *et al.*[4] For the negative charge states, our results show that the stable position of oxygen is exactly the T$_{\text{Ga}}$ interstitial site. In this position, the O atom bonds equally with four gallium first neighbors. These results are different from those reported by Taguchi and Kageshima, which suggest a configuration with oxygen located slightly away from the T$_{\text{Ga}}$ site, bonding with two gallium first neighbors. We believe this configuration cannot be supported by a two-Ga-atom bonding structure, because, apparently, there is no driving force to cause a small motion of the O atom away from the T$_{\text{Ga}}$ site breaking two O-Ga bonds. It is important to note that the electronic structure of the O$_i^0$ defect, with the O atom at the T$_{\text{Ga}}$ site, shows singlet states into the band gap. Therefore, Jahn-Teller distortions are not expected in any charge state.

IV. SUMMARY

We have investigated the structural properties, formation energies, and electronic structure of oxygen at interstitial sites and occupying an arsenic site in GaAs, using pseudopotential total-energy calculations. For the substitutional defect in negative charge states we find off-center oxygen distortions. Our results indicate stable positions for the O atom with C$_{2v}$ symmetry for the 2− and 3− charge states. However, for the 1− charge state we found two equilibrium positions for oxygen, with T$_d$ and C$_{2v}$ symmetries, which are very close in energy. The arsenic-site position is 0.09 eV higher in energy than the off-center position. The calculated formation energies reveal that the off-center substitutional defect forms a negative-U system, where the paramagnetic 2− charge state is never stable.

For the interstitial defect we find three equilibrium positions for the O atom: (i) between an As-Ga pair bonding with each atom in a bridge structure, (ii) at the T$_{\text{Ga}}$ interstitial site bonding with four Ga atoms and, (iii) at the the T$_{\text{As}}$ interstitial site bonding with four As atoms. In neutral charge state the (i) and (ii) equilibrium positions are the stable and the lowest-energy metastable, respectively. However, for 2− and 3− charge states the stable position of the O atom is found in the T$_{\text{Ga}}$ interstitial site (ii), while the lowest-energy metastable position is found between the As-Ga pair (i). Moreover, we find that the 1− charge state is never stable, suggesting that the O$_i$ defect also exhibits a negative-U behavior.

Finally, we conclude that the off-center substitutional oxygen in 1−, 2− and 3− charge states are the responsible for the A, B', and B bands of the LVM absorption spectrum, respectively. For the interstitial oxygen, we find that different stable configurations are formed according to the charge state of the system. The As-O-Ga bridge structure in

p-type and semi-insulating GaAs, and oxygen at the T_{Ga} interstitial site bonding with four neighboring Ga atoms, in *n*-type GaAs. Therefore, we predict a change in the stable configuration going from neutral to negative charge states. This change in the oxygen coordination forms an additional negative-*U* system, now for the interstitial defect, where the $1-$ charge state in never stable.

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