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O^- in GaP: a negative-U centre

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Abstract. We have determined the equilibrium configurations of O^+, O^0 and O^- states for O in GaP using a self-consistent semi-empirical method. A centred configuration is found for both the O^+ and the O^0 states, consistent with experimental results, while the O^- state has the O atom heavily lattice relaxed from its original O^0 state. The energy barrier between the metastable centred O^- and the stable heavily lattice-relaxed off-centred O^- is only 0.12 eV, small enough to be compatible with experimental findings, with the defect levels (+/0) and (0/−) exhibiting an inversion in the ordering. Thus, a negative-U behaviour is demonstrated here and a charge-transfer reaction is postulated for O^- in the GaP system to account for the large lattice relaxation upon capture of the second electron.

1. Introduction

Some time ago, a brief report was made on the electron spin resonance (ESR) measurements of GaP crystals grown with a small amount of Ga_2O_3 and tellurium [1] in which Toyotomi and Morigaki observed a resonance line due to the oxygen impurities. Recently, newly discovered or reconsidered properties of O in GaP compounds have renewed interest in its properties [2]. Dean *et al* [2] in a discussion of their experimental work on the negatively charged O^- donor (two-electron state) in GaP argued that the centred O^- must be metastable with respect to the heavily lattice-relaxed (off-centred) rebonded form of O^-, revealed some time ago in photocapacitance experiments [3–5]. The lattice-relaxed state exhibits a binding energy for the second electron which is much greater than that for the first, resulting in an inversion in the ordering of the defect levels (+/0) and (0/−), with the (+/0) above (0/−). In such a system, the large lattice relaxation is enough to overcome the normal electron–electron repulsion. Thus, the properties of the equilibrium state of O^- in GaP as mentioned above make it an example of a negative-U centre [2, 6, 7], one of the few experimentally established for compound semiconductors [7, 8]. Calculations based on large-scale self-consistent Green function pseudopotential theory [9] have also predicted the centred weakly distorted O^- state to be metastable, but the heavily lattice-distorted rebonded O^- state still remains inaccessible to theoretical studies [2]. However, the ESR measurements of Toyotomi and Morigaki [1] appear to be contradictory to this negative-U behaviour. Hence, this phenomenon is of great interest as its solution may provide greater insight into the nature of deep impurity states and also the lattice distortion and recombination processes involving these states. Moreover, its close relation to the off-centred O in GaAs which has also been experimentally established to be a negative-U centre [7] may shed more light on the metastability of defects [8].

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Very recently, Jones and Oberg [10] showed that O in GaAs can exist in an extraordinarily large number of five different charge states, with the +, 0 and − charge states of O in GaAs exhibiting similar behaviour in terms of geometrical configuration to O in GaP. However, mention should be made that some characteristics of O in GaP may not coincide with those of O in GaAs, e.g. not all the vibrational modes of O in the five different charge states of +, 0, −, 2− and 3− have been observed in both GaP and GaAs. We chose to study O in GaP because experimental evidence for O^+, O^0 and O^- states in GaP is well documented [2–5] but not for O in GaAs in these three charge states. Thus, comparisons of findings for O in two different III–V compound systems should be treated as complementary as a guide to expected results rather than as definitive for both systems.

In this paper, we report the first theoretical calculations of the equilibrium state of the heavily lattice-relaxed rebonded form of O^- (two-electron state) in GaP. Comparison with the total energies of the equilibrium O^0 (one-electron) and O^+ charge states reveals an inversion in the ordering of the defect levels (+/0) and (0/−) with the former above the latter, consistent with experimental findings [3–5] from photocapacitance experiments. Thus, our calculations theoretically demonstrate the negative-U character of O^- in GaP and support the proposals of Dean *et al* [2].

2. Review of experimental and theoretical results on O in GaP

The relevant information regarding the negative-U character of O^- in GaP as well as its charge-state configuration derived from experiments [2–5] and theory [9] is summarized below.

(a) The two levels in the gap, (+/0) at $E_v+1.48$ eV and (0/−) at $E_v+0.24$ eV associated with the one-and two-electron states of O in GaP, respectively, exhibit the inverted ordering characteristic of a negative-U system similar to that for interstitial B in Si [11].

(b) The defect can exist in three charge states: O^+, O^0 (neutral) and O^-. The geometry of the ground states for O^+ and O^0 places the O atom on a substitutional P site, retaining the full tetrahedral symmetry and equidistant from each of its four Ga nearest neighbours [9, 12, 13]. After capture of the second electron, a large lattice relaxation leads to the equilibrium rebonded O^- state. The barrier between the metastable state of the unrelaxed O^-, before the large lattice distortion sets in, and the heavily lattice-relaxed O^- state is small [2].

3. Calculation

3.1. Theoretical method

We employ a semi-empirical self-consistent molecular orbital theory, the complete neglect of differential overlap (CNDO) method [14], in our calculations. In this method, approximations are systematically applied to the matrix elements of the Hartree–Fock–Roothaan equations via three semi-empirical parameters: the orbital exponent, the electronegativities and a bonding parameter. Self-consistent solutions are obtained analogous to Hartree–Fock solutions and the results yield the one-electron energies, total energy, wavefunctions and Mulliken charges. The CNDO method has a good record in defect studies [15–23], especially in cases where total energies are needed or when there is charge transfer [16–19], for instance in the investigation of the diffusion of charged self-interstitials in Si and Ge via the

Bourgoin–Corbett [24] mechanism. The total energy calculated by this method is not merely the sum of the one-electron energies but is calculated to account correctly for electron–electron repulsion [16]. Therefore, the total energies obtained from a series of calculations can yield a potential energy surface of a defect at various sites in a lattice and can also show the effects of lattice relaxation on defect behaviour. The MOSES code [25] is implemented in our calculations and the basis set includes the 4s and 4p orbitals of Ga and the 3s and 3p orbitals of P. The parameters for GaP have been fitted to experimental values of the valence band width, cohesive energy and interatomic spacing, and the calculated bulk properties using this set of parameters are in good agreement with experimental data [22]. These parameters have also been used in our theoretical studies of interstitial H in crystalline GaP [22] where, in the equilibrium configuration, H occupies an interstitial site at a distance of 1.44 Å from a substitutional P atom, in good agreement with the experimental P–H bond length of 1.43 Å in the PH molecule [26]. In addition, they have also been used in our investigation on desorption of Ga atoms [27] and particle emission from defect sites [28, 29] on the GaP(110) surface, where the surface reconstruction of the surface cluster yielded a value of 24.4° for the bond angle tilt, slightly smaller than the experimental value of 27.5° [29]. The parameters for O are from the work of Pople and Beveridge [14]. Our calculations are performed on a 74-atom substitutional site-centred cluster similar to but larger than those (65-atom clusters) used to study defects in Ge and Si [16–21], with an O atom replacing a P atom at the central substitutional site. To take care of the effects of the dangling bonds at the edges of the cluster, these dangling bonds are saturated by hybrid pseudoatoms of Ga or P whose parameters reproduce their relative charges of 0.75 and 1.25, respectively, as well as maintain the constancy of the charges of the atoms around the central region of the cluster [22]. In our calculations, we consider only the isolated O impurity in a perfect GaP crystal and only the atomic relaxations of the substitutional O atom and its four Ga nearest-neighbour atoms are considered in determining the equilibrium configuration for O in three different charge states: O^+, O^0 and O^-.

3.2. Negative-U consideration

The negative-U concept is attributed to Anderson [6] and has been demonstrated for the vacancy in Si [30, 31] and the adatom–substrate bond on the GaAs(110) surface [32]. We first define the defect levels ϵ in terms of the differences in total energies, where $E^q(n)$ represents the total energy of the defect with occupancy n (= 0, 1 or 2 for a bond) electrons in a charge q state. Therefore,

$$\epsilon(+/0) = E^0(1) - E^+(0) \tag{1}$$

$$\epsilon(0/-) = E^-(2) - E^0(1). \tag{2}$$

It is the respective ordering of these levels which defines whether a system exhibits a positive- or a negative-U behaviour. In the normal ordering of levels as in free atoms, one should expect $\epsilon(0/-) > \epsilon(+/0)$ as the electron–electron repulsion U_e comes into play for $\epsilon(0/-)$ as n changes from 1 to 2. Thus, the effective U, which is given by $\epsilon(0/-) - \epsilon(+/0)$, is approximately U_e (positive) if the electron–electron interaction dominates, with negligible lattice distortion. However, the gain in energy by introducing a second electron can sometimes be offset if the lattice relaxation E_l is large enough to overcome the Coulomb repulsion of the two electrons so that

$$U = U_e - E_l. \tag{3}$$

If E_1 is sufficiently large, U is effectively negative so that $\epsilon(0/-)$ is less than $\epsilon(+/0)$, leading to an inversion in ordering, with the difference being the magnitude of the effective U. Therefore,

$$E^-(2) - E^0(1) < E^0(1) - E^+(0) \tag{4}$$

$$E^-(2) + E^+(0) < 2E^0(1) \tag{5}$$

implying that, after capture of the second electron, the two-electron state with each electron in a different bond is unstable with respect to the state with occupancy 0 or 2 on the same bond. Thus, it proceeds spontaneously into the situation where there is electron pairing to eliminate unpaired spins with the accompanying lattice relaxation to overcome the Coulomb repulsion during electron pairing, with the reaction to the left in equation (5) exothermic. For O in GaP, the neutral state O^0 is a one-electron state ($n = 1$), with $n = 0$ and $n = 2$ for O^+ and O^- states, respectively. Thus, by calculating the total energy values for the different charge states and substituting them into equations (1) and (2), the effective U can be determined for O^- in GaP.

4. Results and discussion

We first determine the total energy profile for the neutral O^0 and O^+ in GaP as the O atom is moved from its substitutional site along the $\langle 001 \rangle$ direction (figure 1) with no lattice relaxation of nearest neighbours. For the neutral state, the total energy profile obtained for this unrelaxed state is shown in figure 2. An off-centred site about 0.6 Å from the centred (substitutional) site appears to give the minimum-energy configuration. However, when further calculations are performed with relaxations of its four nearest-neighbour Ga atoms with O at several sites along the $\langle 001 \rangle$ direction, the global minimum-energy configuration is obtained for O^0 when the O is at the centred site with its four Ga nearest neighbours relaxing inwards by about 0.4 Å, lower in energy than the relaxed off-centred site by 2.6 eV (see figure 2). This is almost exactly the difference between the radii of the O atom and the P atom that it replaces [33] and is consistent with other calculations [9]. Examination of the highest occupied molecular orbitals (HOMOs) shows the electron localized on the Ga–O–Ga bonds of two of the Ga nearest-neighbour atoms (Ga_c and Ga_d) and the O atom (table 1), with the coefficients of the basis functions of the HOMO state belonging to these two Ga atoms predominant followed by those belonging to O.

Table 1. Mulliken charge densities of the four Ga nearest-neighbour atoms and O atom for the equilibrium configurations of the centred and off-centred sites for both the one- and the two-electron states.

	Mulliken charge density		
	Charge state, 0 (one-electron state)	Charge state, −1 (two-electron state)	
	Centred	Centred	Off-centred
O	6.27	6.23	6.41
Ga_a	2.67	2.65	2.55
Ga_b	2.66	3.02	2.55
Ga_c	2.89	2.77	3.11
Ga_d	2.89	2.77	3.11

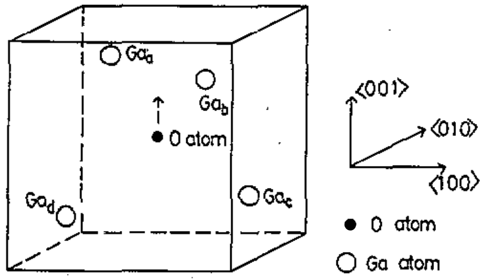

Figure 1. Centred configuration of the substitutional O in GaP with its four nearest-neighbour Ga atoms. The arrow indicates the direction of displacement of the O atom away from its centred site along $\langle 001\rangle$ (z in figure 2). In its relaxed centred state, the four Ga nearest neighbours relax inwards by 0.4 Å, of the order of the difference between the radii of the O atom and the P atom that it replaces.

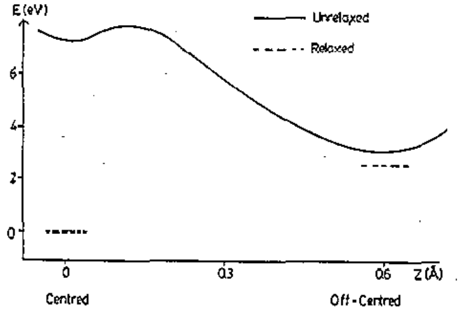

Figure 2. Configuration-coordinate diagram for motion of the O atom along the $\langle 001\rangle$ direction (z) away from its centred site (unrelaxed). The broken lines indicate the total energy levels of the O atom at both the centred and the off-centred sites after atomic relaxations of nearest neighbours.

The corresponding calculation for the O^+ state has its equilibrium configuration at the centred site. Moreover, for both the O^+ and the O^0 cases, the motion of the O atom along the other two major axes, $\langle 011\rangle$ and $\langle 111\rangle$, does not lead to any appreciable lowering in the total energy. Thus, the centred site in which the T_d symmetry is maintained is the equilibrium configuration for both the O^+ and O^0, consistent with experiments [12, 13] and theory [9]. Calculations for O in GaAs for these two charge states also yield this configuration [10].

We then assign a charge of -1 to our cluster to simulate the two-electron state (O^-) for O in GaP. We repeat our calculations, similar to those for the neutral state, to obtain the equilibrium configuration for O^- in GaP with the lowest energy by relaxing the four Ga nearest neighbours as the O atom is moved from the centred site to an interstitial site along the $\langle 001\rangle$ direction. Before implementing this additional lattice relaxation, the minimum-energy configuration has the O atom located at the centred site; displacement of the O atom along the other two major axes, $\langle 011\rangle$ and $\langle 111\rangle$, also does not lead to any lowering of the total energy. However, when additional nearest-neighbour relaxations are taken into consideration in the two-electron state, the global minimum-energy equilibrium configuration is attained when the O atom relaxes to the off-centred site, located at about 0.6 Å along the $\langle 001\rangle$ direction from the (substitutional) centred site. In this global equilibrium configuration, atoms Ga_c and Ga_d also move outwards by 0.3 Å away from their original inward-relaxed positions, i.e. these two Ga atoms and the O atom appear to repel each other for the O^- state. The atoms Ga_a and Ga_b also relax outwards slightly, but not by as much as for Ga_c and Ga_d, perhaps by just enough to accommodate the approaching O atom at the off-centred interstitial site. The energy barrier between the centred site and the heavily lattice-relaxed site of O^- is only about 0.12 eV. This small energy barrier is consistent with experimental findings [2]. Thus, our results demonstrate clearly that the off-centred heavily lattice-relaxed site is the equilibrium configuration for O^- while the centred site applies for O^0 and O^+, compatible with experimental findings [2–5, 12, 13]. The O^- atom at the centred site is therefore metastable with respect to the off-centred site upon capture of the second electron, in accord with equation (5).

We then substitute the total energy values calculated for the equilibrium configurations of the three different charge states of O in GaP into equations (1) and (2) and obtain an effective

$U \simeq -2.8$ eV, comparable with the estimated -1.6 eV derived from photocapacitance spectroscopy experiments [3–5]. Therefore, the inversion in the ordering occurs with $\epsilon(0/-) < \epsilon(+/0)$. Thus, the O^- state in GaP is a negative-U system and theoretically confirms the experimental findings of Kukimoto *et al* [3].

Examination of the coefficients of the basis functions of the HOMOs for O^- reveals the two-electron state essentially localized on Ga_c and Ga_d atoms (see table 1), with the coefficients of the basis functions belonging to Ga_c and Ga_d dominant on HOMOs. It appears that Ga_c and Ga_d form a separate submolecular unit with the O atom repelled towards the more positive Ga_a and Ga_b atoms to rebond with them. The Ga–Ga bond length is 3.3 Å, larger than the value of 2.4 Å [10] for O in GaAs, while the Ga–O bond length is 1.9 Å, slightly larger than the value of 1.7 Å calculated for O in GaAs [10], but compatible with the bond length of 1.9 Å in Ga_2O_3 [34]. These discrepancies could be system specific as the substituted P atom is smaller in radius than the As atom that the O atom replaces and GaP has a smaller lattice constant than GaAs.

The situation for the O^- state in our case, however, may be elucidated as follows. Examination of the Mulliken charge densities of the O atom together with its four nearest-neighbour Ga atoms in the final state configuration (see table 1) of the one- and two-electron states suggests a possible charge-transfer mechanism between the four Ga nearest-neighbour atoms of the O atom upon capture of the second electron from one Ga atom to another with the ensuing lattice relaxation. From table 1, upon capture of the second electron for O^- in the metastable centred configuration, the ensuing lattice distortion leads to charge transfer from atom Ga_b to atoms Ga_c and Ga_d where the first electron is originally localized. Thus, the energy cost in putting the second electron there is offset by the energy gain of the lattice during relaxation. Thus, we may postulate the reaction

$$Ga_b^- + (O + Ga_c + Ga_d)^- \rightarrow Ga_b^0 + (O + Ga_c + Ga_d)^{2-} \qquad (6)$$

to be exothermic. The net negative charge gained by Ga_c–O–Ga_d bonds where the first electron is already localized then repels the anion O^- and Ga_c–Ga_d submolecular unit away from each other, with the O atom displaced to an off-centred rebonded site closer to the more positive Ga_a and Ga_b atoms.

With regards to the earlier report of ESR measurement of O impurities in GaP crystals [1], ESR data are by themselves insufficient to determine the defect structures as certain paramagnetic states of defects have been known to be stabilized by the presence of other defects or impurities [35–37]. For instance, from optical absorption and luminescence experiments [38, 39], the paramagnetic 'primary $Tl^0(0)$' defect [36] in alkali halide crystals undoubtedly exists but extensive searches have so far failed to yield its ESR spectrum. However, other types of Tl^0 defect in association with negative-ion vacancies (monovacancies and divacancies) exhibit ESR spectra easily observable at low temperatures [36]. Our calculations suggest that the isolated O impurity, O^0 (one-electron state), in a perfect GaP crystal should be unstable because of the negative-U nature of the O^- state. Presumably, analogous to the isolated primary Tl^0 defect [36], it could also be stabilized by other defects or impurities. Interestingly, an electron paramagnetic resonance signal has been observed for powders of III–V compounds exposed to oxygen below room temperature [37]. This signal has been shown to be from O_2^- ions which others have found on the surfaces of SiO_2, MgO and ZnO [40–42]. We speculate that the ESR signal observed in [1] could be caused either by the O_2^- ion or by the O impurity in association with other defects or impurities. On the other hand, our calculations focus entirely on an isolated O impurity in the perfect GaP crystal, in the absence of other defects or impurities, and demonstrate that O^- is a negative-U centre, consistent with results from photocapacitance experiments [2–5].

5. Conclusion

We have performed a series of calculations on O in GaP for three different charge states, $+$, 0 and $-$, with O^0 and O^- states corresponding to the one- and two-electron states, respectively. The equilibrium configurations for the three charge states have the O atom at the centred site for O^+ and O^0 states, consistent with experiments [12, 13] while the heavily lattice-relaxed off-centred site applies for the O^- state, with the centred site for O^- metastable upon capture of the second electron according to equation (5), also in agreement with experimental observations [3–5]. The calculated total energies for the three charge states have established the off-centred configuration for O^- to be a negative-U centre, providing the theoretical verification of experimental findings [3–5], with $\epsilon(0/-) < \epsilon(+/0)$. The energy barrier between the metastable centred site and stable off-centred site for the O^- state is also very small, compatible with experimental findings [2]. Our calculations also show that the first electron is essentially localized in part of the Ga–O bonds of two of the nearest neighbours of the centred O. However, upon capture of the second electron, the centred O^- configuration becomes metastable and the exothermic reaction in equation (6), where localization of the two electrons in the Ga–O bonds of O with Ga_c and Ga_d occurs, is postulated as the origin of the consequent large lattice relaxation, leading to O rebonding with Ga_a and Ga_b to overcome the electron–electron repulsion. Our postulated mechanism to account for the origin of the negative-U correlation energy (the large lattice relaxation) may have implications for other off-centred negative-U systems, e.g. O in GaAs [7, 10]. Future theoretical work along this line is envisaged so as to provide further insight into the nature of metastability of defect structures in semiconductors in addition to complementing other theoretical (see, e.g. [10]) and experimental findings.

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