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1996 J. Phys.: Condens. Matter 8 11069

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Structural properties and reorientation of the $\text{H}_2\text{-As}_{\text{Ga}}$ complex in gallium arsenide: a theoretical study

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Received 24 July 1996, in final form 12 September 1996

Abstract. Three vibrational frequencies have been recently observed in hydrogenated GaAs and assigned to the localized modes of two H atoms in a $\text{H}_2\text{-As}_{\text{Ga}}$ complex whose geometry, however, has not been identified. In the present study, the structural, electronic and vibrational properties of a number of configurations of the $\text{H}_2\text{-As}_{\text{Ga}}$ complex have been investigated by performing first-principles total energy calculations. Although the best agreement between theoretical and experimental results has been found in the case of the stable configuration, the geometry of the $\text{H}_2\text{-As}_{\text{Ga}}$ complex could not be definitively established because a metastable configuration may also account for the experimental frequencies. The reorientation of the $\text{H}_2\text{-As}_{\text{Ga}}$ complex in the stable configuration has been subsequently investigated and suggestions have been made for experiments based on infrared-absorption spectroscopy involving application of stress which can resolve the uncertainty as regards the above two configurations.

1. Introduction

The isolated As antisite As_{Ga} in GaAs where an As atom is located on a Ga site has attracted a great deal of attention because it is related to the microscopic structure of the fascinating and technologically important EL2 centre in gallium arsenide. The EL2 centre is a deep defect which behaves as a double donor and shows a well known metastability (for a review of the EL2 properties, see references [1] and [2]). The hydrogen passivation of the EL2 centres has also been reported and explained in terms of the formation of H-As_{Ga} complexes [3, 4]. A recent paper has reported two close high-frequency lines at 1773 cm^{-1} and 1764 cm^{-1} and one lower-frequency line at 779 cm^{-1} , which have been observed by infrared-absorption spectroscopy measurements on hydrogenated GaAs grown at low temperature under As-rich conditions [5]. The presence of As antisites in the material investigated and some similarities with the vibrational properties of the H_2^* complex in silicon [6, 7] led the authors of that paper to the tentative assignment of the two higher frequencies and of the lower frequency to two stretching modes and to one wagging mode, respectively, of two H atoms in a $\text{H}_2\text{-As}_{\text{Ga}}$ complex. However, no information was given on the geometry of the di-hydrogen complex.

Generally, the observation of hydrogen localized vibrational modes (LVM) gives useful information on the microscopic structure of complexes formed by hydrogen and defects or dopants, the hydrogen vibrational frequencies being closely related to the H bonding geometry [8]. In the case of the EL2 defect, however, the LVM analysis is more difficult because two H atoms may be located at different sites around an As_{Ga} (see figure 1), thus giving rise to a variety of configurations for a $\text{H}_2\text{-As}_{\text{Ga}}$ complex. In particular, a recent

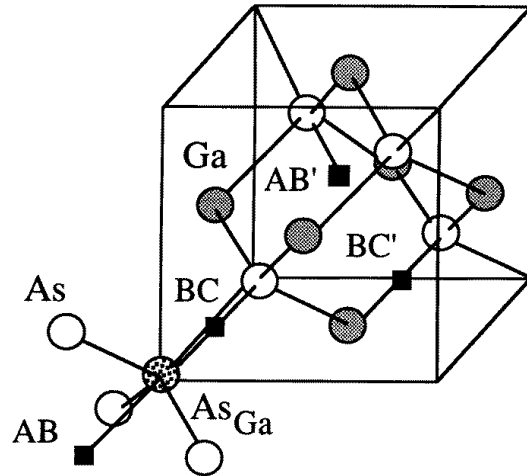


Figure 1. Different hydrogen sites around an As antisite in GaAs (As_{Ga}) are indicated in the figure by solid squares: the antibonding site on the As_{Ga} side, AB; the bond-centred site of an As_{Ga} -As bond, BC; the antibonding site on the As side of a Ga-As bond, AB'; and the bond-centred site of a Ga-As bond, BC'.

theoretical study of the hydrogen passivation of the EL2 defects [9] has shown that the hydrogen atoms may be bonded to: (i) the As_{Ga} ; (ii) the As_{Ga} and one of its As neighbours; and (iii) two As neighbours of the As antisite. Furthermore, preliminary calculations of the hydrogen vibrational frequencies corresponding to the stable and metastable configurations of the H_2 - As_{Ga} complex (see configurations I and II in figure 2, respectively) have shown that both of the configurations can account for the measured vibrational frequencies [10]. The metastable configuration II shows similar H bonding patterns which could account well for the two close H stretching frequencies experimentally observed. The stable configuration I has different H bonding patterns which, however, give rise to a sort of *accidental degeneracy* of the H stretching frequencies, thus also explaining the experimental findings.

In the present work, the structure and the chemical bonding of a reasonably complete set of configurations of the H_2 - As_{Ga} complex have been analysed in detail. This analysis has allowed us to identify several common characteristics for the configurations having a certain degree of stability and has revealed the existence of a metastable configuration—see the configuration III in figure 2—close in energy to the stable one. The electronic and vibrational properties of the stable configuration I and of the two metastable configurations II and III have also been investigated and compared with the experimental findings. Although the best agreement between the theoretical and the available experimental results has been found in the case of the stable configuration I, the metastable configuration II cannot be definitively ruled out on the grounds of the present results. The reorientation of the dihydrogen complex in the stable configuration has therefore been investigated. The results achieved indicate that infrared-absorption spectroscopy measurements involving application of a uniaxial stress could definitively resolve the uncertainty as regards the configurations I and II. They also lead to the prediction of an energy barrier of about 0.6 eV to the motion of one H atom around the As antisite.

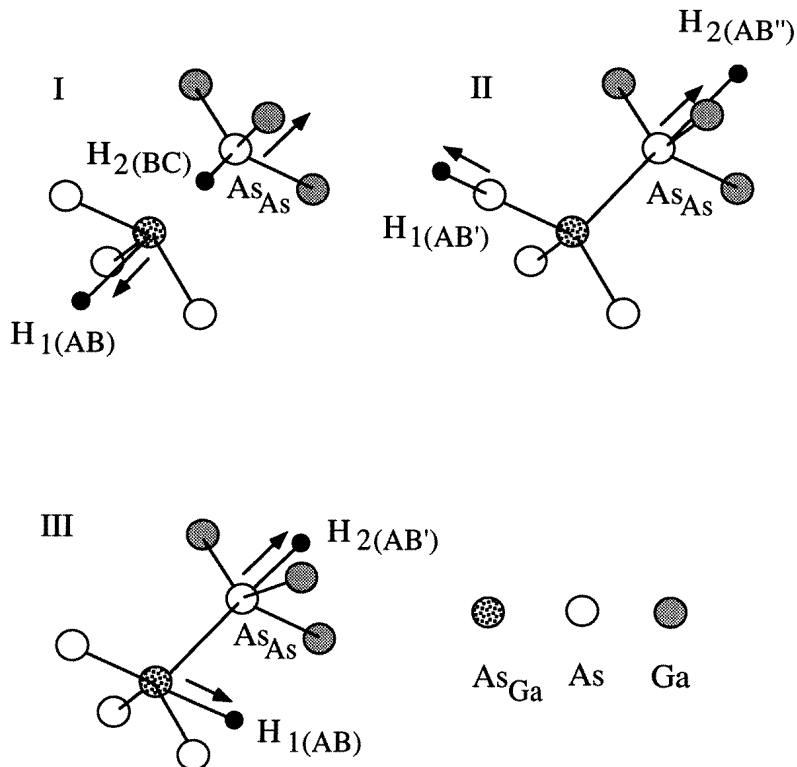


Figure 2. Geometries of three configurations of the di-hydrogen complex (see the text): (I) the stable $As_{Ga}-H_2^*$ configuration formed by one As antisite, As_{Ga} , two H atoms located at an AB site and a BC site along a same (111) axis (see also figure 1), and As_{As} , the As neighbour of the As_{Ga} aligned with the H atoms and the As antisite; (II) a metastable configuration with the H atoms located at two antibonding sites, AB' and AB'', with the next two As atoms neighbouring the As_{Ga} ; and (III) a metastable configuration close in energy to the stable one, where the H atoms are located at an AB site and an AB' site (see the text). The arrows indicate the directions of the displacements of the As_{Ga} and of the As atoms involved in the complex with respect to the perfect-lattice positions.

2. Methods

The equilibrium geometries of several di-hydrogen configurations have been taken from reference [9]. Further configurations have been investigated by performing *ab initio* total energy calculations in the local density functional (LDF) framework and in the supercell approach [11, 12]. The equilibrium geometries of the di-hydrogen configurations have been calculated by minimizing the Hellmann–Feynman forces on the atoms [13]. The exchange–correlation functional of Ceperley and Alder [14] has been used together with norm-conserving pseudopotentials [15] and plane-wave basis sets; k -space integration has been performed with the use of the special-points technique [16, 17].

The hydrogen vibrational frequencies have been evaluated in two different ways. In the former, one H atom is moved away from its equilibrium position while the other atoms of the supercell are frozen in the positions of the minimum-energy configuration, i.e., it is assumed that the H motion is independent of that of the other atoms. The frequencies of the

hydrogen LVM were then estimated in the harmonic approximation by fitting to a parabola the total energy values corresponding to the different H positions. This procedure has been used successfully in the case of complexes formed by hydrogen and shallow defects in crystalline Si (c-Si) [18, 19] and GaAs (c-GaAs) [20, 21]. In a different approach, the normal modes of the atoms in the di-hydrogen complex have been calculated in order to investigate a possible coupling between the atomic motions [22–25]. The total energy has been expressed in terms of a quadratic form of the bond-stretching and bond-bending displacements from the equilibrium positions of the atoms in the complex. The elements of the force-constant matrix have been calculated by taking the second derivative of the energy with respect to the interatomic displacements. The dynamical matrix has been then calculated and diagonalized to obtain the normal vibrational modes and the corresponding eigenvectors. Tests on the number of interatomic displacements included in the calculations have also been performed to take into account the effects of the motion of the atoms neighbouring the complex. The present results have been achieved by including seven interatomic displacements in the calculations. Convergence tests on the total energy values have been performed as in reference [9]. Satisfactorily converged values have been achieved by using 32-atom supercells, the (4, 4, 4) k -point mesh and a cut-off of 12 Ryd.

A rough estimate of the position of the electronic states related to the di-hydrogen complex has been obtained by taking a weighted average of the electronic eigenvalues over several high-symmetry points in the Brillouin zone. The passivation of the EL2 defect has been investigated by calculating the occupancy levels relative to the highest occupied electronic state of the complex. The occupancy levels have been evaluated by following the approach of Baraff *et al* [26].

Table 1. Atomic displacements, bond lengths and total energies of the stable and metastable di-hydrogen configurations shown in figures 2 and 3 (see the text). In the case of the configuration II, the $\Delta\text{As}_{\text{Ga}}$ and the $\text{As}_{\text{Ga}}\text{-H}_1$ values must be referred to the As atom bonded to the H_1 atom. The directions of the atomic displacements (ΔX) from the perfect-GaAs-lattice positions are shown in figures 2 and 3 for each configuration. All of the geometrical values are given in ångströms. The length of the $\text{As}_{\text{Ga}}\text{-As}_{\text{As}}$ bond should be compared with the value estimated for an $\text{As}_{\text{Ga}}\text{-As}$ bond in the case of the isolated As_{Ga} (i.e., without H), 2.55 Å. The total energies E of the different configurations are given in eV by assuming the stable configuration as the zero of energy.

Configuration	$\Delta\text{As}_{\text{Ga}}$	$\Delta\text{As}_{\text{As}}$	$\text{As}_{\text{Ga}}\text{-As}_{\text{As}}$	$\text{As}_{\text{Ga}}\text{-H}_1$	$\text{As}_{\text{As}}\text{-H}_2$	E
I	0.71	0.27	3.41	1.56	1.61	0.00
II	0.45	0.45	2.90	1.61	1.61	0.35
III	0.59	0.65	2.87	1.64	1.57	0.10
IV	0.44	0.24	3.11	1.59	1.57	0.37
V	0.59	0.26	2.87	1.57	1.65	0.38
VI	0.50	0.34	2.58	1.62	1.68	0.40
VII	0.80	0.56	3.78	1.56	1.56	0.48

3. Results and discussion

3.1. Structural and electronic properties of di-hydrogen configurations

In ‘perfect’ GaAs, an *isolated* H atom behaves as an acceptor when located at an antibonding site on the As side of a Ga–As bond, AB' , and as a donor when located at a bond-centred site of a Ga–As bond, BC' ; see figure 1 [27]. The AB' and BC' sites are stable or metastable

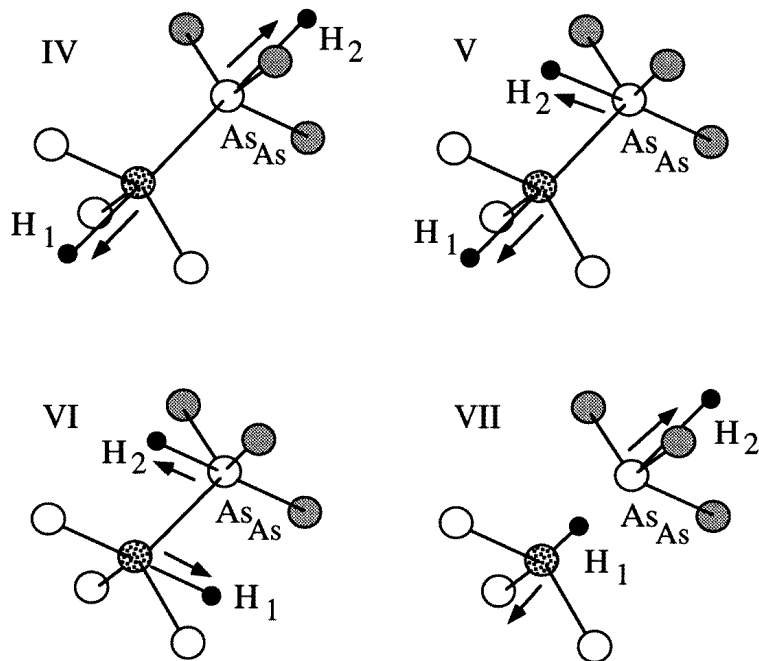


Figure 3. Geometries of different metastable configurations of the di-hydrogen complex (see the text). The arrows indicate the directions of the displacements of the As_{Ga} and of the As atoms involved in the complex with respect to the perfect-lattice positions.

depending on the position of the Fermi level. Around an As antisite (see figure 1), the antibonding site on the As_{Ga} side, AB, is stable, and the bond-centred site of an $As_{Ga}-As$ bond, BC, the AB' and the BC' sites are metastable, while several low-symmetry sites are unstable [9]. When *two* H atoms are located near to an As antisite to form a complex which should lead to the donor neutralization, the antibonding sites (AB and AB') should be the most likely H sites because of the acceptor behaviour of hydrogen at these sites. The BC sites of the $As_{Ga}-As$ bonds should also be taken into account as possible H sites because the H behaviour in these sites is unknown. However, the BC' sites can be ruled out due to the donor behaviour of hydrogen, together with the low-symmetry sites which are unstable. Configurations with H atoms far from the As_{Ga} may also be disregarded since a strong interaction between the hydrogen atoms and the As antisites is needed in order to account for the EL2 passivation [8, 9]. A reasonable selection of the possible configurations for a di-hydrogen complex can therefore be obtained by considering the following two cases: (a) two H atoms located at two antibonding sites, AB or AB' ; and, (b) one H atom located next to a BC site and the other one located at an AB or AB' site. All of the non-equivalent di-hydrogen configurations corresponding to the two cases above are reported in figures 2, 3 and 4. Figure 2 shows the stable configuration and the two most interesting metastable configurations. Figures 3 and 4 show further metastable configurations and four unstable configurations, respectively. Details of the geometries of the stable and metastable configurations are given in table 1. The directions of the displacements of the As atoms in the complex with respect to their unrelaxed positions are shown in figures 2 and 3.

The stable configuration of the H_2-As_{Ga} complex—see the configuration I in figure

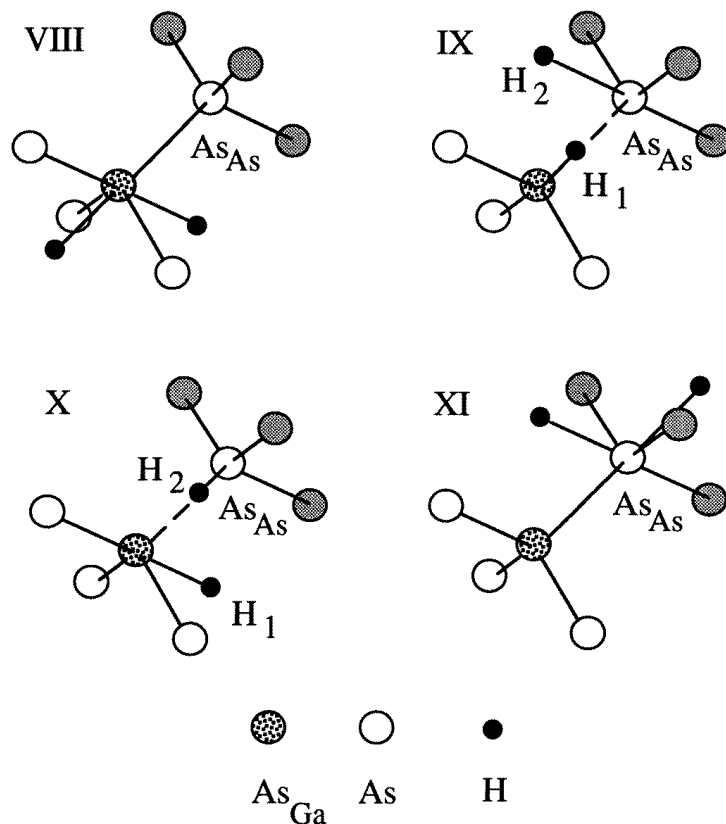


Figure 4. Geometries of four unstable configurations of the di-hydrogen complex (see the text).

2—is similar to that of the H_2^* defect in c-Si [28] and c-GaAs [29] and is characterized by two H, one As_{Ga} and one As (As_{As} in figure 2) atoms located along the same [111] axis. It will hereafter be referred to as $As_{Ga}-H_2^*$. In figure 2 and hereafter, As_{As} indicates a particular As neighbour of the As antisite involved in the formation of the di-hydrogen complex. In the same figure, the two H atoms located at an AB site and a BC site will be referred to as H_{AB} and H_{BC} or as H_1 and H_2 , respectively (similarly, the H atoms in the other configurations will be referred to as H_1 and H_2 or identified by the sites at which they are located). In this configuration, both of the H atoms form strong H–As bonds. This is shown by the $H_{AB}-As_{Ga}$ and $H_{BC}-As_{As}$ bond lengths (see table 1), which are slightly longer than the H–As bond length in the arsine molecule (1.52 Å), and by a sizeable piling up of the electron charge density between the H and the As atoms; see figure 5(a). At variance with the case of H in ‘perfect’ GaAs, the H atom located at the BC site *does not behave as a donor* because it *saturates* the As_{As} dangling bond and forms a strong $H_{BC}-As_{As}$ bond instead of the three-centre $Ga-H_{BC}-As$ bond which characterizes the H donor behaviour in ‘perfect’ GaAs [27]. The As_{Ga} atom moves away from the As_{As} to form a $H_{AB}-As_{Ga}$ bond; see figure 2 and table 1. It is close to the plane formed by the other three As neighbours, thus being characterized by an sp^2 hybridization. The plot of the electronic charge density given in figure 5(a) shows a small but appreciable charge density piling up between the As_{Ga} and the H_{BC} atoms which indicates an additional, weak bonding interaction between

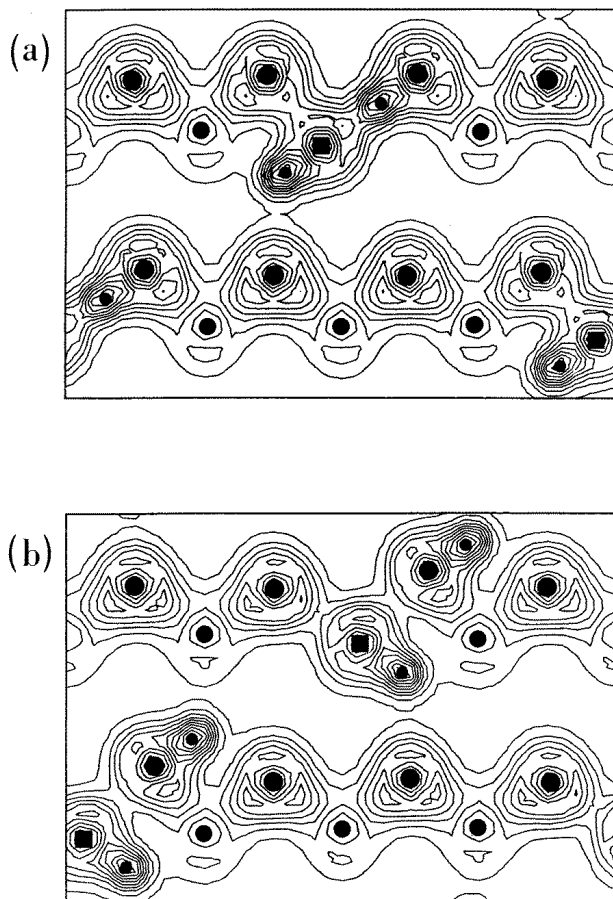


Figure 5. Contour plots in the (110) plane of the electronic charge density for: (a) the stable $As_{Ga}-H_2^*$ configuration—see the configuration I in figure 2—and (b) the metastable configuration III of figure 2 (see the text). The atomic positions are indicated by a solid square corresponding to the As_{Ga} and by solid circles of different sizes corresponding, from the largest to the smallest, to the As, Ga and H atoms, respectively.

these atoms. This interaction favours the sp^2 hybridization and a fivefold coordination of the As_{Ga} atom, thus stabilizing the $As_{Ga}-H_2^*$ complex. It is worth noticing that the double-donor state in the energy gap induced by an *isolated* As antisite is antibonding with respect to the $As_{Ga}-As_{As}$ bonds [9]. Thus, the *breaking* of the $As_{Ga}-As_{As}$ bond caused by the formation of the $H_{BC}-As_{As}$ bond lowers the defect state in energy (by favouring the EL2 passivation) and further stabilizes the complex. Similar effects are given by the reduction of the electronic charge on the As_{Ga} induced by the formation of the $H_{AB}-As_{Ga}$ bond (the H_{AB} behaves as an acceptor) and by the weak $As_{Ga}-H_{BC}$ bonding interaction [9]. Three conditions seem therefore to stabilize the $As_{Ga}-H_2^*$ configuration: (i) the fivefold coordination and the sp^2 hybridization of the As_{Ga} atom; (ii) the breaking of the $As_{Ga}-As_{As}$ bond; and (iii) a charge transfer from the As_{Ga} to the H_{AB} and H_{BC} atoms. The relevance of these conditions for the structural stability of the di-hydrogen configurations has been confirmed by an analysis

of the structure and the chemical bonding of all of the configurations reported in figures 2–4, whose results will be briefly discussed in the following.

For the first condition, a sixfold-coordinated As atom is never stable as in the configurations VIII and XI in figure 4, where the $\text{As}_{\text{Ga}}\text{--As}_{\text{As}}$ bond is stretched but not broken. In the unstable configuration IX in figure 4, the As_{As} atom is fivefold coordinated but the sp^2 hybridization is hindered by the presence of the H_1 atom which pushes the As_{As} atom away along the $\text{As}_{\text{Ga}}\text{--As}_{\text{As}}$ axis, thus making difficult its displacement toward the H_2 atom located along a different [111] direction. Similar considerations hold for the unstable configuration X in figure 4. On the other hand, the metastable configurations of figures 2 and 3 are characterized by the sp^2 hybridization and the fivefold coordination of the As atoms involved in the complex, thus indicating that both of the conditions must be realized to achieve a certain degree of stability. Furthermore, the different degrees of stability of the metastable configurations seem to be related to the different degrees of fulfilment of the above conditions. For instance, the configuration VI is high in energy because a full sp^2 hybridization of the As_{Ga} would require a contraction of the $\text{As}_{\text{Ga}}\text{--As}_{\text{As}}$ bond (the length of this bond is 2.55 Å for the isolated As antisite). The other two conditions related to the stability of the $\text{As}_{\text{Ga}}\text{--H}_2^*$ complex—points (ii) and (iii) above—are also mostly satisfied in the metastable configurations of figures 2 and 3. As an example, a charge transfer from the As_{Ga} atom to ‘acceptor’ H atoms located at antibonding sites (AB or AB’) is realized in all of the metastable configurations.

The above discussion may be continued by giving some detail on the structure and the stability of the configurations II and III. The stability of the configuration II has been investigated with particular care due to its interesting H bonding patterns. Geometries of this configuration slightly different from that given in figure 2 have also been investigated, where the two H atoms bonded to the As_{Ga} neighbours are located at AB’ sites not aligned with the $\text{As}\text{--As}_{\text{Ga}}$ bond axes. Different starting geometries have also been used in the total-energy-minimization procedure in order to avoid problems of local minima. The geometry given in figure 2 turned out to be the lowest in energy with respect to similar geometries and 0.35 eV higher in energy than the stable one. This result seems consistent with the previous considerations on the stability of the di-hydrogen configurations. In fact, the sp^2 hybridization of the two As atoms in the complex is less pronounced than that of the As_{Ga} in the stable configuration (see the atomic displacements of the As atoms in table 1) and the absence of an H_{AB} atom bonded to the As_{Ga} may result in a less efficient charge transfer from the As_{Ga} to the H atoms.

Finally, the present investigation of the di-hydrogen configurations has revealed that a metastable configuration, i.e., the configuration III of figure 2, has a total energy close to that of the stable configuration (see table 1). This can be accounted for by the following characteristics of the configuration III: (a) the conditions of fivefold coordination and sp^2 hybridization are satisfied to a larger extent than in the other metastable configurations (see the atomic displacements of the As atoms in table 1); (b) the $\text{As}_{\text{Ga}}\text{--As}_{\text{As}}$ bond, broken in the stable configuration, is significantly weakened in the configuration III as shown by an increase of $\approx 12\%$ of its length and by the charge-density plot given in figure 5(b); and (c) the charge transfer from the As antisite to the H atoms is realized in an efficient way due to the presence of two H_{AB} acceptors and of the $\text{H}_{\text{AB}}\text{--As}_{\text{Ga}}$ bond; see again figure 5(b).

The electronic structure of the stable configuration I has been investigated in a previous study [9]. The electronic structures of the metastable configurations II and III have been investigated here in order to verify whether their atomic arrangements may lead to the EL2 passivation. The electronic structure of a di-hydrogen complex is characterized by two electronic levels which accommodate the two electrons of the As_{Ga} double-donor level and

the two electrons of the two H atoms. In the case of the configuration II, an analysis of the electronic eigenvalues shows that one level is located near the top of the valence band while the second one is 0.48 eV higher in energy. In the case of the configuration III, one level is located near the top of the valence band and the second level is 0.12 eV higher in energy. For comparison, in the stable configuration both levels are in the valence band (thus accounting for the EL2 passivation) [9]. The occupancy levels of the highest occupied electronic state of the complex have been evaluated by considering a system formed by the di-hydrogen complex and a reservoir of non-interactive electrons with an energy per particle equal to the Fermi energy [26]. The zero of energy corresponds to all valence band states occupied and all levels above the valence band empty, namely to a $(++)$ charge state of the complex. The occupancy levels give the value of the Fermi energy for which the ground-state occupancy changes from 0 to 1 or from 0 to 2, thus corresponding to the transitions $(++/+)$ and $(++/0)$, respectively. In the case of the configuration II, the two occupancy levels are located at ≈ 0.4 eV above the top of the valence band, thus indicating that this configuration does not lead to the EL2 passivation. In the case of the configuration III, the two occupancy levels are very close and are located at ≈ 0.06 eV above the top of the valence band. This indicates that the EL2 defect is mostly passivated in this configuration because the $(++)$ and the $(+)$ charge states of the complex would be stable only in highly doped p-type GaAs, when the Fermi level is located at less than 0.06 eV from the top of the valence band. For comparison, in the case of the stable configuration, an analysis of the occupancy levels indicates that the $(+)$ and $(++)$ charge states are never stable (i.e., the EL2 defect is certainly passivated) [9].

3.2. H vibrational frequencies and H_2-As_{Ga} complex reorientation

The H vibrational frequencies observed experimentally [5] are characterized by two very close stretching frequencies and by a single wagging frequency related to the motions of the two H atoms of the H_2-As_{Ga} complex; see table 2. In the cases of the configurations I, II and III, the H vibrational frequencies evaluated by calculating the normal modes of the complex and by assuming an independent motion of the H atoms are given in the fourth and fifth columns of table 2, respectively.

Among the possible configurations of the di-hydrogen complex, the configuration II in figure 2 deserves particular attention because it shows similar H bonding patterns which may explain the closeness of the experimental stretching frequencies. A similar geometry has been recently proposed for a Pt- H_2 complex in crystalline silicon where two close H stretching frequencies have been also measured [30]. For this configuration, the marked differences between the estimates of the vibrational frequencies given by the two different procedures reveal a coupling between the H vibrational modes; see table 2. The normal-modes analysis shows that the five atoms in the complex may give rise to four A_1 modes and three B_1 modes in the plane of the complex. The corresponding vibrational frequencies cannot be degenerate because the symmetry group of the complex, C_{2v} , has only one-dimensional representations. The H vibrations are mainly associated with an A_1 symmetric stretching mode at 1640 cm^{-1} , to a B_1 asymmetric stretching mode at 1545 cm^{-1} , to one B_1 wagging mode at 880 cm^{-1} and to one A_1 wagging mode at 408 cm^{-1} . The two stretching frequencies and the highest wagging frequency approach the experimental ones within 7%, 12% and 13%, respectively, which corresponds to a satisfactory agreement with the experimental frequencies, if it is taken into account that an accuracy of $\approx 10\%$ is typical of the present theoretical methods [6, 18–21, 24, 31, 32]. However, this accuracy leads to stretching frequencies that are not so close as the experimental ones, their difference being

Table 2. Frequency values for the H local modes in the stable configuration I and in the metastable configurations II and III of the $\text{H}_2\text{-AsGa}$ complex (see the text and figure 2). Normal-mode frequency values (ν_{NM}) and frequency values calculated by assuming an independent motion of the H atoms (ν) are given in the fourth and fifth columns of the table, respectively. The vibrational frequencies for the H modes in the H_2^* complex in c-Si (also given in the table) are taken from reference [6]. The experimental results reported in the bottom part of the table are taken from reference [5]. All values are given in cm^{-1} .

Configurations	Bonds	Modes	ν_{NM}	ν
I	$\text{H}_{AB}\text{-AsGa}$	Stretching	1760	1747
		Wagging	681	669
	$\text{H}_{BC}\text{-AsAs}$	Stretching	1633	1623
		Wagging	624	634
II	$\text{H}_{AB'}\text{-AsAs}$	Stretching	1640	1615
		Wagging	880	772
	$\text{H}_{AB''}\text{-AsAs}$	Stretching	1545	1615
		Wagging	408	772
III	$\text{H}_{AB}\text{-AsGa}$	Stretching	1540	1550
		Wagging	720	723
	$\text{H}_{AB'}\text{-AsAs}$	Stretching	1810	1825
		Wagging	650	634
H_2^*	$\text{H}_{AB}\text{-Si}$	Stretching		1480
		Wagging		690
	$\text{H}_{BC}\text{-Si}$	Stretching		2070
		Wagging		220
Experiment		Stretching	1773	
		Stretching	1764	
		Wagging	779	

$\approx 100 \text{ cm}^{-1}$ against the value of 9 cm^{-1} given by the experiment. A possible problem with this configuration is represented by the observation of just one H wagging mode. Two wagging modes are indeed expected because the frequencies of H wagging modes predicted by theory in the case of H atoms located at antibonding sites have been actually observed [19, 20, 24, 31].

In the stable AsGa-H_2^* configuration, an analysis of the normal modes gives three Σ stretching modes and two doubly degenerate Π wagging modes corresponding to the motion of the atoms in the complex, in agreement with the $\text{C}_{\infty v}$ symmetry of this linear configuration. One low-frequency Σ mode is related to the motion of the two As atoms in the complex. A symmetric stretching mode at 1760 cm^{-1} is predominantly associated with the vibration of the H_{AB} atom. An asymmetric stretching mode at 1633 cm^{-1} is instead dominated by the vibration of the H_{BC} atom. The stretching frequency of the $\text{H}_{AB}\text{-AsGa}$ bond is higher than that of the $\text{H}_{BC}\text{-AsAs}$ bond, in agreement with the corresponding dissociation energy values, 2.8 eV and 2.3 eV, respectively [9]. Likewise, the higher wagging mode value corresponds to the motion of the H_{AB} atom. Quite similar results are found in the case of the independent motion of the H atoms (see the last column in table 2), thus indicating a scarce coupling between the vibrational modes of the atoms of the complex. The stretching frequencies of 1760 cm^{-1} and 1633 cm^{-1} approach within 0.7% and 7% the corresponding experimental values, thus still corresponding to a satisfactory agreement between theory and experiment [6, 18–21, 24, 31, 32]. Theory also gives two different H wagging frequencies against the single wagging frequency observed experimentally. However, previous experimental and theoretical studies have shown that a H atom next to a

BC site may give rise to wagging modes which are not detected in infrared measurements [7, 20, 33–35]. The calculated H_{AB} wagging frequency, 681 cm^{-1} , approaches the experimental one (779 cm^{-1}) within 12%, which also corresponds to a satisfactory agreement with the experimental results. Although the H_{AB} and H_{BC} atoms have different bonding patterns, the difference between the corresponding stretching frequencies is comparable with that estimated in the case of the configuration II. This surprising result can be accounted for by the peculiar bonding of the H_{BC} atom which gives rise to a sort of *accidental degeneracy* of the two H stretching frequencies, as can be shown by a comparison of the structural and vibrational properties of the As_{Ga} - H_2^* complex with those of the H_2^* complex in crystalline silicon [6, 7]. The H_2^* complex is formed by two Si atoms of a Si–Si bond (Si_1 and Si_2 , which correspond to the As_{Ga} and As_{As} atoms of the configuration I, respectively) and two H atoms located at the BC and AB sites, like in the case of the configuration I. The bond length of the H_{BC} - Si_2 bond, 1.53 \AA , is smaller than that of the H_{AB} - Si_1 bond, 1.62 \AA , thus suggesting that the former bond is stronger than the latter one [6, 7]. Correspondingly, the stretching frequency of the H_{BC} - Si_2 bond is *higher* than that of the H_{AB} - Si_1 one; see table 2. Incidentally, it may be noted that *only one wagging mode* is observed for this complex, which is attributed to the motion of the H_{AB} atom [7]. Although the atomic arrangement of the H_2^* complex in Si is quite similar to that of the As_{Ga} - H_2^* complex, the H_{BC} atoms in the two complexes have a quite different chemical bonding. A weak bonding interaction like the As_{Ga} - H_{BC} one is indeed absent in the case of the H_2^* complex in silicon, as shown by a comparison of the plots of the charge-density distribution given in figure 5(a) for the former complex and in reference [6] for the latter one. The As_{Ga} - H_{BC} bonding interaction is due to the presence of an excess of charge on the As antisite and to the possibility of fivefold coordination of the As atom. These two characteristics are absent in the silicon case where the Si_1 atom has no electronic charge in excess and is *fourfold* coordinated with the H_{AB} and its three Si neighbours. The As_{Ga} - H_{BC} bonding interaction weakens the H_{BC} - As_{As} bond whose bond length is *larger* than that of the H_{AB} - As_{Ga} bond, *at variance* with the case of the H_{BC} - Si_2 and H_{AB} - Si_1 bonds in the H_2^* complex. Correspondingly, the order of the stretching frequencies relative to the H_{AB} and H_{BC} atoms in the As_{Ga} - H_2^* complex is *inverted* with respect to that found in the H_2^* complex in Si, the stretching frequency relative to the H_{AB} atom now being the higher one; see table 2. *This inversion may lead to an accidental degeneracy* for the H stretching frequencies, which can account for the experimental results. The peculiar chemical bonding of the H_{BC} atom in the As_{Ga} - H_2^* complex is further confirmed by a comparison with the stretching frequencies calculated for an *isolated* H atom located at a BC' site or at an AB' site in 'perfect' GaAs. These frequencies are equal to 2400 cm^{-1} and 1600 cm^{-1} , respectively [27], thus still showing an inverted order with respect to that found in the case of the As_{Ga} - H_2^* complex.

Finally, the H vibrational frequencies for the configuration III have been estimated in order to establish whether this configuration may account for the observed frequencies; see table 2. The values calculated by assuming a H motion independent of that of the heavier atoms are quite close to those given by the normal-mode analysis, thus indicating a small coupling between the H vibrational modes. The stretching frequency of the H_{AB} - As_{As} bond is higher than that of the H_{AB} - As_{Ga} bond, in agreement with the corresponding dissociation energy values, 2.2 eV and 1.6 eV , respectively, which have been estimated as in reference [9]. These results and the H–As bond lengths given in table 1 indicate that the bond formed by hydrogen and the As_{Ga} is weaker than that involving the As_{As} neighbour, at variance to what was found in the case of the configuration I. This can be accounted for by the fact that the As_{Ga} - As_{As} bond is not completely broken in the configuration III, thus leaving an excess of electronic charge on the As antisite which leads to a longer and weaker H_{AB} - As_{Ga}

bond; see table 1. The agreement of the calculated frequencies with the experimental ones is satisfactory, the two stretching frequencies and the higher wagging frequency approaching within 2%, 13% and 8% the experimental ones, respectively. However, the difference between the H stretching frequencies, 270 cm^{-1} , corresponds to the worst agreement with the experimental results. Furthermore, *two wagging frequencies* should be observed in this configuration (as for the configuration II) due to the presence of two H atoms located at antibonding sites, at variance with the experimental findings.

The results concerning the structural, electronic and vibrational properties of the configurations I, II and III may be summarized as follows: (a) the different stabilities of the three configurations are coherent with the three conditions (i)–(iii) above accounting for the different stabilities of all of the configurations investigated; (b) the H stretching frequencies evaluated for the three configurations agree to the same extent with the experimental results within the accuracy of the theoretical methods used (a slightly better agreement is found for the stable configuration); (c) the closeness of the experimental stretching frequencies is better approximated only in the cases of the configurations I and II (where the two frequencies could be brought closer together by slight changes in the total energy surface which would be within the accuracy of the theoretical methods); (d) the observation of a single H wagging frequency may be accounted for only in the case of the configuration I; and (e) the EL2 passivation is certainly achieved only in the case of the configuration I. The present results favour therefore the stable $\text{As}_{\text{Ga}}\text{-H}_2^*$ configuration, although the accuracy of the calculated vibrational frequencies is not such as to allow us to rule out the metastable configuration II. Further investigations have therefore been performed to provide suggestions for experiments which could resolve the uncertainty as regards these two configurations. Before describing these experiments, we should recall some results achieved by infrared-absorption spectroscopy measurements performed with application of a uniaxial stress in the cases of complexes having a H atom located at a BC site [36, 37, 38], e.g., the $\text{Si}_{\text{As}}\text{-H}_{\text{BC}}\text{-Ga}$ complex in GaAs [38]. In that case, due to the presence of four equivalent BC sites around the Si_{As} , the H_{BC} atom can have its threefold axis along any of the (111) crystal axes. A stress applied along a (110) direction can lower the symmetry of the crystal and partially lift this orientational degeneracy. This causes the H stretching band to split into components because the vibrational transition energies of differently oriented complexes are no longer equivalent [36–38]. The experiment can be performed if there is an appreciable energy barrier to the motion of the H_{BC} atom around the Si_{As} to occupy another BC site of a neighbour $\text{Si}_{\text{As}}\text{-Ga}$ bond. In that case, the measurement is performed at sufficiently low temperature to avoid the reorientation of the hydrogen complex. The experiment has been successful in the case of the $\text{Si}_{\text{As}}\text{-H}_{\text{BC}}\text{-Ga}$ complex where a splitting of the H stretching band has been observed and an energy barrier of 0.26 eV to the complex reorientation has been found [38]. Similar splittings cannot be observed for H atoms located at antibonding sites which are not affected by an applied stress.

The configuration I of figure 2 presents an orientational degeneracy similar to that of the $\text{Si}_{\text{As}}\text{-H}_{\text{BC}}\text{-Ga}$ complex. Thus, it can give rise to a splitting of the H_{BC} stretching frequency upon application of stress if there is an appreciable energy barrier to the complex reorientation. This energy barrier needs to be investigated because it could be quite low due to the existence of a metastable configuration close in energy to the stable one. A reorientation involving a simultaneous motion of the two H atoms in the complex and leading from the configuration I to the configuration III seems unlikely. Thus, the motions of the H_{AB} and H_{BC} atoms may be analysed separately. The motion of the H_{AB} atom around the As_{Ga} toward another AB site would lead to the unstable configuration X of figure 4. It should therefore be preceded by the motion of the H_{BC} atom. An inspection of the figures 2

and 3 shows that the simplest path for the motion of the H_{BC} atom is around the As_{As} atom to reach the AB site of the H_2 atom in the configuration V. The energy barrier to this motion has a lower bound of 0.38 eV, i.e., the relative energy of the configuration V; see table 1. It has been investigated by selecting several supercell geometries where the H_{BC} atom is located at different points of a circular path around the As_{As} , which connects the starting and ending sites of the H atom. The selected path is on a (110) plane and has a radius equal to 1.65 Å (i.e., the $H_{AB}-As_{As}$ distance in the configuration V). Each supercell geometry has been relaxed by moving all of the atoms except the H atom on the circular path. The highest total energy value along this path has been obtained at about midway between the initial and the final positions of the H atom. In correspondence with this maximum of energy, a radial path has been considered in order to optimize the H- As_{As} distance. This procedure finds an energy barrier to the H_{BC} motion equal to 0.6 eV, which is significantly larger than the value found in the case of the $Si_{As}-H_{BC}-Ga$ complex and seems therefore suitable for observing a frequency splitting in experiments performed at low temperature upon application of a stress. Moreover, upon application of stress, effects of the H_{BC} motion on the vibrational spectra should be observed on increasing the temperature. In particular, when the H_{BC} atom moves, the close stretching frequencies observed without stress should be replaced by quite different frequencies probably related to the configuration III, which is the most stable among the configurations without H_{BC} atoms. The configuration II is not affected by an applied stress. Thus, the suggested experiments can distinguish between the stable configuration I and the metastable configuration II.

4. Conclusions

The structural properties of a number of configurations of a complex formed by two H atoms and one As antisite have been carefully analysed. It has been found that the stability of these configurations is related to: (i) the fivefold coordination and the sp^2 hybridization of the As_{Ga} atom and the As atoms involved in the complex; (ii) the breaking or the weakening of the $As_{Ga}-As_{As}$ bond; and (iii) a charge transfer from the As_{Ga} to the H atoms in the complex. The electronic and vibrational properties of the stable and two metastable di-hydrogen configurations have also been investigated and compared with experimental findings. Although the best agreement between theory and experiment has been found in the case of the stable $As_{Ga}-H_2^*$ configuration, the geometry of the complex corresponding to the measured H frequencies has not been firmly identified because a metastable configuration may also account for the experimental results. Reorientation-like mechanisms of the complex in the stable configuration have therefore been investigated and an energy barrier to the H motion has been evaluated in order to provide suggestions for infrared-absorption spectroscopy measurements involving application of uniaxial stress which can resolve the uncertainty as regards the above two configurations.

Acknowledgment

It is a pleasure to acknowledge R E Pritchard for very helpful discussions.

References

- [1] Dabrowski J and Scheffler M 1988 *Phys. Rev. Lett.* **60** 2183; 1989 *Phys. Rev. B* **40** 10 391
- [2] Spaeth J M, Krambrock K and Hofmann D M 1990 *The Physics of Semiconductors* vol 1, ed E M Anastassakis and J D Joannopoulos (Singapore: World Scientific) p 441

- [3] Lagowski J, Kaminska M, Parsey J M Jr, Gatos H C and Lichtensteiger M 1982 *Appl. Phys. Lett.* **41** 1078
- [4] Omel'yanovskii E M, Pakhomov A V and Polyakov Ya A 1987 *Sov. Phys.-Semicond.* **21** 514
- [5] Pritchard R E, McQuaid S A, Hart L, Newman R C, Mäkinen J, von Bardeleben H J and Missous M 1995 *J. Appl. Phys.* **78** 2411
- [6] Chang K J and Chadi D J 1990 *Phys. Rev. B* **42** 7651
- [7] Holbech J D, Bech Nielsen B, Jones R, Sitch P and Öberg S 1993 *Phys. Rev. Lett.* **71** 875
- [8] Pankove J I and Johnson N M (ed) 1991 *Hydrogen in Semiconductors (Semiconductors and Semimetals 34)* (San Diego, CA: Academic)
- [9] Amore Bonapasta A 1995 *Phys. Rev. B* **51** 4172
- [10] Amore Bonapasta A 1996 to be published
- [11] Lundqvist S and March N H (ed) 1983 *Theory of the Inhomogeneous Electron Gas* (New York: Plenum)
- [12] Martin R M 1985 *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter* ed J T Devreese and P Van Camp (New York: Plenum)
- [13] Hellmann H 1937 *Einführung in die Quantumchemie* (Leipzig: Deuticke)
- Feynman R P 1939 *Phys. Rev.* **56** 340
- [14] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
- Perdew J and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [15] Andreoni W, Pastore G, Car R, Parrinello M and Giannozzi P 1989 *Band Structure Engineering in Semiconductor Microstructures (NATO Advanced Study Institute, Series B: Physics, vol 189)* ed R A Abram and M Jaros (New York: Plenum) p 129
- [16] Baldereschi A 1973 *Phys. Rev. B* **7** 5212
- Chadi D J and Cohen M L 1973 *Phys. Rev. B* **8** 5747
- Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [17] A computer code based on the theoretical methods used here has been developed in collaboration with Dr P Giannozzi (Scuola Normale Superiore, Pisa, Italy), who also tuned a version of the package for a CRAY-C92 system.
- [18] Van de Walle C G, Denteneer P J H, Bar-Yam Y and Pantelides S T 1989 *Phys. Rev. B* **39** 10791
- [19] Denteneer P J H, Van de Walle C G and Pantelides S T 1990 *Phys. Rev. B* **41** 3885
- [20] Pavese L and Giannozzi P 1991 *Phys. Rev. B* **43** 2446
- [21] Amore Bonapasta A 1993 *Phys. Rev. B* **48** 8771
- [22] Goldstein H 1965 *Classical Mechanics* (Cambridge, MA: Addison-Wesley)
- [23] Wilson E B, Decius J C and Cross P C 1955 *Molecular Vibrations* (New York: McGraw Hill)
- [24] Zhang S B and Chadi D J 1990 *Phys. Rev. B* **41** 3882
- [25] Northrup J E 1989 *Phys. Rev. B* **39** 1434
- [26] Baraff G A, Kane E O and Schluter M 1980 *Phys. Rev. B* **21** 5662
- [27] Pavese L, Giannozzi P and Reinhart F K 1990 *Phys. Rev. B* **42** 1864
- [28] Chang K J and Chadi D J 1989 *Phys. Rev. Lett.* **62** 937
- [29] Pavese L and Giannozzi P 1992 *Phys. Rev. B* **46** 4621
- [30] Uftring S J, Stavola M, Williams P M and Watkins G D 1995 *Phys. Rev. B* **51** 9612
- [31] Amore Bonapasta A, Giannozzi P and Capizzi M 1990 *Phys. Rev. B* **42** 3175
- [32] For comparison with the results of other theoretical methods, in the case of the H_2^* complex in silicon (see reference [7]), *ab initio* local density cluster methods have given estimates of the H_{AB} and the H_{BC} stretching frequencies approaching the experimental values within 0.3% and 7%, respectively, while the estimate of the H_{AB} wagging mode was in error by about 23%.
- [33] Jones R and Öberg S 1991 *Phys. Rev. B* **44** 3673
- [34] DeLeo G G and Fowler W B 1991 *Hydrogen in Semiconductors (Semiconductors and Semimetals 34)* ed J I Pankove and N M Johnson (San Diego, CA: Academic)
- [35] A transverse E mode has been reported in the case of the $H_{BC}-C_{As}$ complex in GaAs which, however, is an unusual complex due to the presence of a pair of light atoms (i.e., H and C); see Davidson B R, Newman R C, Bullough T J and Joyce T B 1993 *Phys. Rev. B* **48** 17106
- [36] Bergman K, Stavola M, Pearton S J and Hayes T 1988 *Phys. Rev. B* **38** 9463
- [37] Stavola M, Bergman K, Pearton S J and Lopata J 1988 *Phys. Rev. Lett.* **61** 2786
- [38] Kozuch D M, Stavola M, Spector S J, Pearton S J and Lopata J 1993 *Phys. Rev. B* **48** 8751