

# Nitrogen passivation by atomic hydrogen in $\text{GaAs}_y\text{N}_{1-y}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{N}_{1-y}$ alloys

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Previous theoretical studies on N-H complexes in GaAsN have been extended here to new di-hydrogen complex configurations and to N-H complexes in the  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$  alloy. Moreover, a deeper analysis has been performed on the structure, formation energies, chemical bonding and electronic properties of old and new N-H complexes in the above alloys. On the ground of the achieved results, the existence of a novel di-hydrogen complex is predicted that is characterized by a  $C_{2v}$  symmetry and peculiar vibrational properties. Complexes with this symmetry are not stable in N-free GaAs. Further, we propose a sound model for the N passivation founded on the characteristics of the electronic states and the local atomic relaxations induced by the N-H complexes. This model explains why the N passivation is not achieved in the case of monohydrogen complexes and realized through the formation of the  $\text{N-H}_2^*$  dihydrogen complexes. Finally, it is suggested that different N-H complexes (and different vibrational spectra) should be observed in hydrogenated *p*-type and *n*-type N-containing alloys.

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## I. INTRODUCTION

Long ago it was discovered that hydrogen irradiation dramatically affects the electronic properties of semiconductors.<sup>1</sup> Hydrogen can diffuse in the semiconductor lattice and readily attach to dangling bonds. Moreover, hydrogen can form chemical complexes with shallow and deep impurities, thus inducing strong changes of the impurity chemical bonding. As a general effect of the hydrogen-defect interaction, nonradiative recombination center, shallow impurity, and deep defect energy levels are wiped out from the gap of crystalline elemental and compound semiconductors. On the other hand, the effects of hydrogen on isoelectronic impurities are almost unknown. Among these impurities, substitutional N in III-V semiconductors has recently received much attention due to the peculiar effects it induces on the properties of the host semiconductor. In GaAs, when the As anion is substituted by an isoelectronic lighter (heavier) atom, an increase (decrease) of the compound energy gap is expected in a virtual crystal approach, as experimentally observed in the case of P (Sb) substitution. However, this simple rule does not hold in the case of N substitution. A giant reduction in the band gap energy has been reported indeed for N concentrations of the order of a few percent in  $\text{GaAs}_y\text{N}_{1-y}$  and  $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{N}_{1-y}$ .<sup>2</sup> Moreover, hydrogen irradiation fully neutralizes the N effects in both the above alloys by restoring the band gap of the N-free semiconductors.<sup>3,4</sup> Since N is an isoelectronic impurity, this latter surprising result cannot be explained in terms of a saturation of dangling bonds or neutralization of chemical valence effects, as usually done in the case of shallow and deep impurities.

The behavior of N in GaAs and the effects of hydrogenation on the GaAsN properties have stimulated several theoretical studies on the formation of N-H complexes in GaAsN and their role in the H neutralization of the N effects.<sup>5-7</sup> In

these papers, the structural properties and the formation energies of different N-H complexes in GaAsN have been investigated. The achieved results show that the formation of monohydrogen and dihydrogen complexes (see Figs. 1 and 2, respectively) depends on the position of the Fermi level, as recently found in the case of Ga(PN).<sup>8</sup> In one study,<sup>6</sup> it is also suggested that H acts as a donor in GaAsN, whereas it is an amphoteric impurity in GaAs. Finally, those studies have shown that *only* the formation of  $\text{N-H}_2^*$  dihydrogen complexes [see Figs. 2(a) and 2(b)] leads to the neutralization of

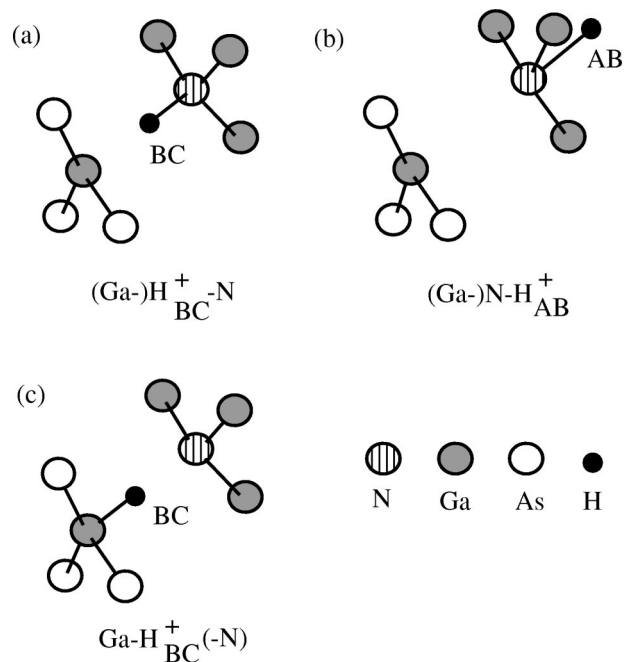


FIG. 1. Atomic configurations of some monohydrogen complexes in  $\text{GaAs}_y\text{N}_{1-y}$ : BC and AB indicate a bond centered and an antibonding site of H, respectively.

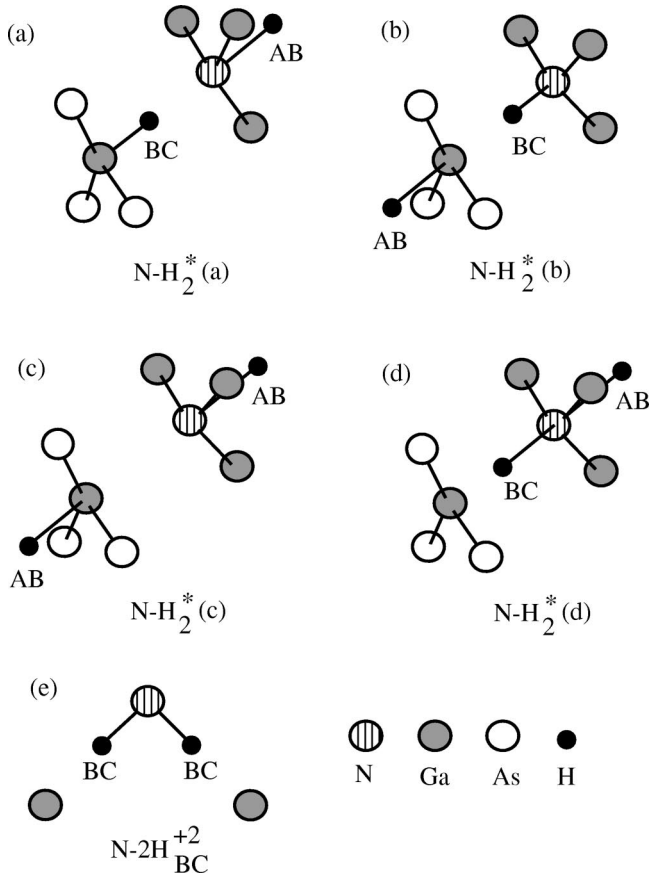


FIG. 2. Atomic configurations of some dihydrogen complexes in  $\text{GaAs}_y\text{N}_{1-y}$ : BC and AB indicate a bond centered and an antibonding site of H, respectively.

the N effects and restores the GaAs energy gap. Despite of this last puzzling and stimulating finding, a model for the N passivation mechanism has not been firmly established yet.<sup>9</sup> In the present study, we extend our previous investigations on N-H complexes in GaAsN (Ref. 7) to di-hydrogen complex configurations different from the  $\text{H}_2^*$  configurations already investigated and to the properties of N-H complexes in InGaAsN. Moreover, the structure and the formation energies of old and new N-H complexes have been carefully analyzed and related to their chemical bonding and electronic properties in order to achieve a sound model for the N passivation. Some stretching frequencies of the local vibrational modes (LVM's) of the hydrogen atoms in the N-H complexes have been also calculated both in GaAsN and InGaAsN. In detail, the N-H complexes have been investigated in the  $\text{GaAs}_{0.97}\text{N}_{0.03}$  and  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$  alloys by first-principles local density functional methods in a supercell approach.

The main results of the present study are summarized here. First, we predict the existence of a novel dihydrogen complex that is characterized by a  $C_{2v}$  symmetry different from the  $C_{\infty v}$  symmetry of the  $\text{H}_2^*$  dihydrogen complexes investigated in the previous studies. It is worth noticing that a similar complex with a  $C_{2v}$  symmetry is not stable in N-free GaAs. It is quite stable instead in GaAsN and InGaAsN and can give rise to peculiar, infrared vibrational

modes that should be revealed by infrared spectroscopy measurements. This complex can also contribute to the nitrogen passivation. Second, a model is proposed for the N passivation by hydrogen that is founded on the bonding or antibonding characters of the electronic levels and a careful analysis of the *local atomic relaxations* induced by the formation of the N-H complexes. This model explains why the N passivation is not achieved in the case of monohydrogen complexes and realized through the formation of the  $\text{N-H}_2^*$  dihydrogen complexes. Third, present results suggest that different N-H complexes and different vibrational spectra should be observed in hydrogenated *p*-type and *n*-type N-containing alloys. Finally, the results obtained for the N-H complexes in InGaAsN parallel those achieved for the N-H complexes in GaAsN, thus indicating that the energetics of these complexes is dominated by the formation of strong N-H bonds.

## II. METHODS

By analogy with the case of defect formation energies,<sup>10</sup> in a supercell approach the formation energy per H atom  $\Omega[\text{N}-n\text{H}]^q$  of a N-*n*H complex involving *n*H atoms and a *q* charge may be written as

$$\Omega[\text{N}-n\text{H}]^q = \frac{1}{n} [E[\text{N}-n\text{H}]^q - E[\text{N}] - n\mu_{\text{H}} + q\mu_e],$$

where  $E[\text{N}-n\text{H}]^q$  is the total energy of a supercell of GaAs containing one N atom and *n* H atoms,  $\mu_{\text{H}}$  is the chemical potential of hydrogen, which is assumed equal to half of the  $\text{H}_2$ -molecule energy in the vacuum, and *q* is the positive (negative) charge on the complex, namely, the number of electrons transferred from (to) the complex to (from) an electron reservoir with a chemical potential (or Fermi level)  $\mu_e$  ( $\mu_e = 0$  corresponds to a Fermi level at the top of the valence band).

The effects of N and H on the GaAs energy gap have been investigated here by calculating the transition energy of a defect, that is, the Fermi-energy value  $\epsilon^{n/n+1}$  for which the occupation number of a defect electronic-state in the energy gap changes from *n* to *n*+1. In turns,  $\epsilon^{n/n+1}$  can be estimated by the Fermi-energy position where the formation energies of the *n* and *n*+1 charge states of the defect are equal.<sup>11</sup> In the present study, the N atoms in the  $\text{GaAs}_{0.97}\text{N}_{0.03}$  and  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$  alloys (i.e., the alloys simulated by 64-atom supercells) as well as the related N-H complexes have been considered as isolated defects and the corresponding  $\epsilon^{n/n+1}$  values have been calculated. The  $\epsilon^{n/n+1}$  values should be compared with the GaAs (InGaAs) energy gap, estimated here by calculating the  $\epsilon^{0/-}$  value in the N-free compound material. Although this method gives a rough estimate of the GaAs and InGaAs energy gap, it permits one to compare consistent results obtained within a same approach and to follow the evolution of the gap induced by the incorporation of N or the formation of N-H complexes. This procedure has been successfully used in the case of defects in AlN.<sup>12</sup> In addition, the  $\epsilon^{+/0}$  value for the Si shallow-donor in GaAs and InGaAs has been calculated here. This donor induces a level close to the bottom of the

GaAs or InGaAs conduction band, thus providing a further state of reference to locate the N and N-H levels in the energy gap.

Total energies have been calculated in the local density approximation (LDA) by using supercells, separable *ab initio* pseudopotentials,<sup>13</sup> planewave basis sets, the special-points technique for  $\mathbf{k}$ -space integration, and the exchange-correlation functional of Ceperley and Alder.<sup>14</sup> Ultrasoft pseudopotentials have been used in the case of nitrogen<sup>15</sup> and nonlinear core corrections have been used in the case of indium. Convergence tests have been done by using plane-wave cutoffs ranging from 18 to 28 Ry, supercells of 32 and 64 atoms, and  $\mathbf{k}$ -point meshes equivalent to a (4,4,4) or (8,8,8) Monkhorst-Pack mesh in the zinc blende unit cell. The results presented here have been achieved by using 64-atom supercells, the (4,4,4)  $\mathbf{k}$ -point Monkhorst-Pack mesh, and cutoffs of 22 Ry. The stretching frequencies of the hydrogen LVM's have been estimated in the harmonic approximation.<sup>16</sup>

In the N-H complexes, the chemical bonding and the nature of the electronic states have been investigated by analyzing plots of the total (valence) electronic charge density and  $|\Psi_{n,0}|^2$  densities. Further details on the methods can be found elsewhere.<sup>10</sup>

### III. RESULTS AND DISCUSSION

#### A. Monohydrogen complexes in GaAsN

The monohydrogen complexes investigated in GaAsN involve the  $H^+$ ,  $H^0$ , and  $H^-$  species, one N atom and its Ga neighbors. Two different cases have been considered for the H sites, which correspond to a H atom located close to the N atom and to the Ga atom of a Ga-N bond, respectively. In the former case, a H atom (ion) has been located at (i) a site close to the bond-centered (BC) site of a Ga-N bond, see Fig. 1(a), (ii) an antibonding site (AB) on the N side, see Fig. 1(b), (iii) a tetrahedral site (Td), i.e., a site located along the Ga-N axis, about 2.40 Å far from the N atom, (iv) some lower symmetry sites not aligned with the Ga-N bond axis. These complexes have been identified, e.g., with the notation  $N-H_{BC}^+(-Ga)$ , see Fig. 1(a), in order to stress the main atoms involved in the complex. In the case of a H atom close to the Ga atom, the BC, AB, and Td sites are located on the side of the Ga atom of a Ga-N bond. The corresponding complexes are identified, e.g., by  $Ga-H_{BC}^+(-N)$ , see Fig. 1(c). The optimized geometries of the most interesting complexes are given in Table I. The table also reports total energy values relative to the energy of the most stable complex for each H species, that is taken equal to zero. The  $N-H_{BC}^+(-Ga)$  complex of Fig. 1(a) is the most stable complex formed by the  $H^+$  ion. This complex is characterized by an on line  $N-H_{BC}^+-Ga$  configuration where the  $N-H_{BC}^+$  and  $Ga-H_{BC}^+$  distances are equal to 1.05 and 2.43 Å, respectively. An estimate of the same distances made by using the atomic covalent radii<sup>17</sup> gives values equal to 1.07 and 1.58 Å, respectively. The comparison of the two sets of values suggests the formation of a strong N-H bond and the existence of a weak Ga-H interaction. In fact, the  $N-H_{BC}^+$  and  $Ga-H_{BC}^+$  distances

TABLE I. Atomic distances, atomic displacements with respect to ideal positions ( $\Delta X$  values), and total energy values of monohydrogen complexes in GaAsN. Positive (negative)  $\Delta X$  values indicate an outward (inward) atomic displacement with respect to the Ga-N chemical bond. Total energy values are relative to the energy of the most stable complex (for each H species) that is taken equal to zero. Distances are given in Å, total energies in eV. In the case of the  $As-H_{BC}^+-Ga$  complex, the  $\Delta As$  and  $As-X$  values are reported in the  $\Delta N$  and  $N-X$  columns ( $X=Ga, H$ ), respectively. NS stands for "not stable." The upper, middle, and lower parts of the table report results for the  $H^+$ ,  $H^0$ , and  $H^-$  species, respectively.

Complex	N-H	Ga-H	Ga-N	$\Delta Ga$	$\Delta N$	E
$[N-H_{BC}^+(-Ga)]$	1.05	2.43	3.48	0.63	0.45	0.00
$[(Ga-)N-H_{AB}^+]$	1.06	4.80	3.74	0.53	0.81	0.24
$[Ga-H_{BC}^+(-N)]$						NS
$[(N-)Ga-H_{AB}^+]$	5.54	1.61	3.93	0.92	0.61	2.67
$[As-H_{BC}^+-Ga]$	1.55	1.82	3.37	0.53	0.44	
$[N-H_{BC}^0(-Ga)]$	1.08	2.11	3.18	0.29	0.49	0.00
$[(Ga-)N-H_{AB}^0]$	1.07	4.40	3.34	0.07	0.87	0.32
$[Ga-H_{BC}^0(-N)]$						NS
$[(N-)Ga-H_{AB}^0]$	5.49	1.61	3.88	0.91	0.56	1.49
$[N-H_{BC}^-(-Ga)]$	1.09	1.95	3.04	0.04	0.63	0.00
$[(Ga-)N-H_{AB}^-]$	1.07	4.14	3.07	-0.34	1.01	0.10
$[Ga-H_{BC}^-(-N)]$	1.93	1.54	3.47	0.18	0.89	0.36
$[(N-)Ga-H_{AB}^-]$	5.36	1.61	3.75	0.89	0.46	0.50

are 3% smaller and 54% larger than those calculated by covalent radii, respectively. These results can be compared with the geometry of the  $As-H_{BC}^+-Ga$  complex formed by a  $H^+$  ion in GaAs, see Table I. In this complex, the  $As-H_{BC}^+$  and  $Ga-H_{BC}^+$  distances are 2 and 15% larger than those estimated by the covalent radii 1.52 and 1.58 Å, respectively, which indicates the existence of some bonding interaction of the  $H_{BC}^+$  ion with *both* the As and Ga atoms. The above results suggest therefore that the three-center bond formed by  $H^+$  in the  $As-H_{BC}^+-Ga$  complex is replaced by a *two-center* N-H bond plus a *dangling bond of the Ga atom* in the  $N-H_{BC}^+(-Ga)$  complex. The deep difference between the chemical bonding of  $H^+$  in the two above complexes is confirmed by the plots of the total (valence) charge density shown in Fig. 3. This figure shows that the considerable electronic charge piled up on an isolated N atom [see Fig. 3(a)] is used to screen the  $H_{BC}^+$  ion [see Fig. 3(b)], thus resulting in a piling up of the charge on the N-H pair and in the formation of a strong N-H bond. A quite different charge distribution is shown in Fig. 3(c), that suggests instead the formation of a three-center  $As-H_{BC}^+-Ga$  bond in pure GaAs. In agreement with this picture, the total energy values calculated for the above complexes show that the N-H bond in the  $N-H_{BC}^+(-Ga)$  complex is 1.2 eV more stable than the As-H bond formed in the corresponding  $As-H_{BC}^+-Ga$  complex.

The tendency of the substitutional nitrogen to form strong N-H bonds is confirmed by the existence of a  $(Ga-)N-H_{AB}^+$  complex [see Fig. 1(b)] only 0.24 eV higher in energy than

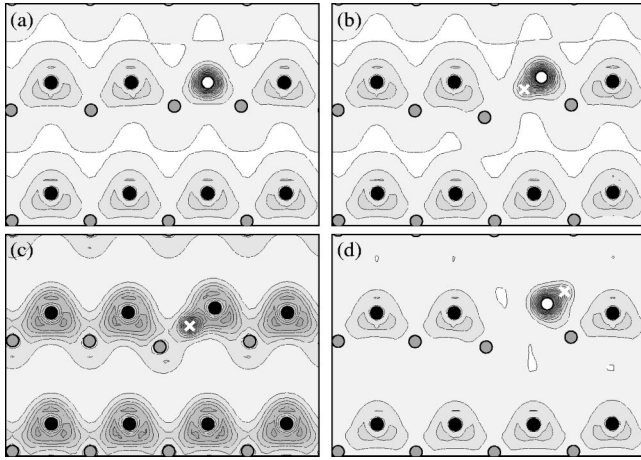


FIG. 3. Contour plots in the (110) plane of the total (valence) charge density corresponding to (a) an isolated N atom, (b) the  $N-H_{BC}^+$  complex, (c) the  $As-H_{BC}^+-Ga$  complex in pure GaAs, and (d) the  $N-H_{AB}^+$  complex. The As, Ga, and N atoms are indicated by black, gray, and white full dots, respectively. Small crosses represent the H atoms.

the  $N-H_{BC}^+(-Ga)$  complex. The  $(Ga)-N-H_{AB}^+$  complex is characterized by a N-H distance of 1.06 Å and by a Ga-N distance of 3.74 Å, that is 86% larger than the value given by the covalent radii (2.01 Å). Furthermore, both Ga and N atoms relax outward (see Table I). The geometry of this complex indicates therefore the formation of a strong N-H bond and the absence of any Ga-N bonding interaction. This picture is confirmed by the corresponding charge density distribution, see Fig. 3(d), that shows a charge piling up on the N-H pair very similar to that of Fig. 3(b). Even the N-H bond in the  $(Ga)-N-H_{AB}^+$  complex results to be 1.2 eV more stable than the As-H bond formed in the corresponding complex in GaAs, where an As atom replaces the N atom. Quite different results have been obtained in the case of complexes where the  $H^+$  ion is bonded to the Ga atom. The  $Ga-H_{BC}^+(-N)$  complex is not stable. The  $H^+$  ion moves from the Ga towards the N atom by reaching the configuration of the  $N-H_{BC}^+(-Ga)$  complex. The  $(N)-Ga-H_{AB}^+$  complex is very high in energy. Finally, the Td sites on the side of N or Ga atoms are not stable for  $H^+$ .

In the case of  $H^0$ , the  $N-H_{BC}^0(-Ga)$  complex is the most stable complex at variance with the case of GaAs, where the most stable complex corresponds to a H atom located at the AB site on the side of the As atom.<sup>18</sup> In the  $N-H_{BC}^0(-Ga)$  complex the H-Ga distance is smaller than that in the  $N-H_{BC}^+(-Ga)$  complex. Accordingly, a reduced Ga atomic displacement characterizes the neutral complex. The results achieved for the other neutral monohydrogen complexes parallel those achieved in the case of  $H^+$ .

Finally, in the case of  $H^-$ , the complex formed by the  $H^-$  ion located at the BC site close to the N site,  $N-H_{BC}^-(-Ga)$ , is once more the most stable one. It is worth noticing that, in this complex, the Ga-H distance and the Ga atomic displacement are further reduced with respect to the corresponding complexes formed by  $H^+$  and  $H^0$ . The  $(Ga)-N-H_{AB}^-$  complex

is only 0.10 eV higher in energy than the  $N-H_{BC}^-(-Ga)$  complex. Further, the  $Ga-H_{BC}^-(-N)$  and  $(N)-Ga-H_{AB}^-$  complexes are more stable with respect to the corresponding complexes formed by  $H^+$  and  $H^0$ .

The stability of the  $N-H_{BC}^-(-Ga)$  complex is quite surprising for two reasons: (i) this result is very different from that achieved in GaAs, where a Td site is the most stable site for  $H^-$  and<sup>18</sup> (ii) it does not agree with a simple model proposed to explain the H properties in GaAs.<sup>19</sup> In this model, hydrogen behaves as a donor or an acceptor depending on the site where it is located. A H atom located at the BC site of a GaAs bond (where there is a piling up of electronic charge) tends to loose its electron, thus inducing a donor level in the GaAs gap. Then, it can give rise to a  $H^+$  ion that is stable at the BC site, where it is screened well by the electronic charge of its Ga and As neighbors, see Fig. 3(c). On the other hand, a H atom at a Td site (that is, in a region poor of electronic charge) tends to reach the stable electronic configuration of He by trapping one electron, thus inducing an acceptor level in the energy gap. Then, it can give rise to an isolated  $H^-$  ion that has the electronic configuration of He, is stable at the Td site and has no interaction with its neighboring atoms.

It is useful now to summarize the differences between the properties of H in GaAsN and GaAs: (i)  $H^+$  forms a strong  $N-H_{BC}^+$  bond in the former material and a three-center  $As-H-Ga$  bond in the latter one, (ii) in the case of  $H^0$ , the BC site is more stable than the AB site in GaAsN, while the opposite is true in GaAs, and (iii)  $H^-$  is an isolated ion at the Td site in GaAs, whereas it forms a  $N-H_{BC}^-$  complex in GaAsN. All these results suggest that the N atom in GaAsN suffers for a lacking of electronic charge. In fact, in the  $N-H_{BC}^+(-Ga)$  complex, N forms a strong N-H bond by subtracting the H ion to a possible  $Ga-H_{BC}^+$  interaction and inducing a dangling bond on the Ga atom. Moreover, a small Ga-H interaction becomes possible only by satisfying the needs of the N atom, that is, by adding some electronic charge to the complex. This is shown by an analysis of the local lattice relaxations occurring in the  $N-H_{BC}^-(-Ga)$  complexes. In these complexes, the Ga-H distance and the Ga atomic displacement decrease indeed on going from the  $H^+$  to the  $H^0$  and  $H^-$  species (in detail, the Ga-H distances and the Ga displacements decrease from 2.43 to 1.95 Å and from 0.63 to 0.04 Å respectively, see Table I). Furthermore,  $H^-$  is not stable at the Td site because the N atom needs more electronic charge than the As atom it substitutes. The N atom forms therefore a strong bond with the negative  $H^-$  ion at variance with the As atom in GaAs. A consequence of the above analysis is that the acceptor character of  $H^0$  in GaAs should be weakened in GaAsN because the negative charge of  $H^-$  is shared with the N atom. In turn, this should affect the negative- $U$  behavior of H, that is, the existence of an H acceptor level in the gap lower than the donor level.<sup>20</sup> An estimate of the negative- $U$  character of H is given by the energy released in the reaction  $2H^0 \rightarrow H^+ + H^-$ . As a matter of fact, this energy has the value of 0.6 eV in GaAs (Ref. 20) and of 0.1 eV in GaAsN, in agreement with the results of the above analysis. The tendency of N to get more electronic

TABLE II. Atomic distances, atomic displacements with respect to ideal positions ( $\Delta X$  values), and total energy values of dihydrogen complexes in GaAsN. Positive (negative)  $\Delta X$  values indicate an outward (inward) atomic displacement with respect to the Ga-N chemical bond. Total energy values are relative to the energy of the most stable complex that is taken equal to zero. Distances are given in Å, total energies in eV. In the case of the Ga-H<sub>1(BC)</sub>-As-H<sub>2(AB)</sub> complex, the  $\Delta$ As and As-X values are reported in the  $\Delta N$  and N-X columns ( $X = \text{Ga, H}$ ), respectively.

Complex	N-H <sub>1</sub>	N-H <sub>2</sub>	Ga-H <sub>1</sub>	Ga-H <sub>2</sub>	Ga-N	$\Delta N$	$\Delta \text{Ga}$	E
[Ga-H <sub>1(BC)</sub> -N-H <sub>2(AB)</sub> ](a)	2.06	1.07	1.54	4.67	3.60	1.04	0.16	0.0
[H <sub>1(AB)</sub> -Ga-H <sub>2(BC)</sub> -N](b)	5.35	1.06	1.59	2.70	3.76	0.43	0.93	0.13
[H <sub>1(AB)</sub> -Ga-N-H <sub>2(AB)</sub> ](c)	5.75	1.06	1.60	5.20	4.14	0.84	0.90	0.53
[Ga-H <sub>1(BC)</sub> -As-H <sub>2(AB)</sub> ]	1.92	1.58	1.65	5.05	3.47	0.84	0.23	
[Ga-H <sub>1(BC)</sub> -N-H <sub>2(BC)</sub> -Ga <sup>+2</sup> ]	1.05	1.05	2.43		3.47	0.66	0.64	

charge and the existence of a weak Ga-H interaction in the N-H<sub>BC</sub>(-Ga) complexes (that increases with the electronic charge on the complex) will be recalled in Sec. III D when discussing the N passivation model.

### B. Dihydrogen complexes in GaAsN

The configurations of the most interesting dihydrogen complexes are shown in Fig. 2. Details of the corresponding geometries and total energy values are given in Table II. In these complexes, the H atoms are located at BC or AB sites close to N or to its Ga neighbors. The most stable complex is the Ga-H<sub>BC</sub>-N-H<sub>AB</sub> complex shown in Fig. 2(a). This complex will be also referred to as N-H<sub>2</sub><sup>\*</sup>(a) because it is characterized by an “on line” H<sub>2</sub><sup>\*</sup>-like configuration, where the two H atoms are bonded to a Ga and an N atom of a Ga-N bond, respectively. In the N-H<sub>2</sub><sup>\*</sup>(a) complex, the N-H<sub>AB</sub> and Ga-H<sub>BC</sub> bond lengths are equal to 1.07 and 1.54 Å (see Table II), respectively, equal and 3% smaller with respect to the corresponding values estimated from covalent radii. The N-H<sub>BC</sub> distance is 2.06 Å, that is 92% larger than the 1.07 Å value estimated from the atomic covalent radii. This complex is therefore characterized by the formation of two strong Ga-H<sub>BC</sub> and N-H<sub>AB</sub> bonds and by a negligible N-H<sub>BC</sub> interaction. This chemical bonding is confirmed by the total charge-density distributions shown in Fig. 4(a). It should be noted the similarity between the charge density distributions around the N-H<sub>AB</sub> bond shown in Figs. 4(a) and 3(d). Even the H<sub>AB</sub>-Ga-H<sub>BC</sub>-N complex shown in Fig. 2(b) has a H<sub>2</sub><sup>\*</sup>-like configuration. It will be also referred to as N-H<sub>2</sub><sup>\*</sup>(b). This complex is only 0.13 eV higher in energy than the N-H<sub>2</sub><sup>\*</sup>(a) complex and presents a quite similar chemical bonding. The geometry of the N-H<sub>2</sub><sup>\*</sup>(b) complex and the corresponding total charge-density distributions [see Fig. 4(b)] show indeed that the complex is characterized by two strong Ga-H<sub>AB</sub> and N-H<sub>BC</sub> bonds and by a negligible Ga-H<sub>BC</sub> interaction. The dihydrogen complex of Fig. 2(c) is further higher in energy. The complex of Fig. 2(d) is unstable, together with the corresponding one having the two H atoms bonded to a Ga atom of the Ga-N bond (not shown in the figure). These two complexes evolve without barriers towards the geometries of the N-H<sub>2</sub><sup>\*</sup>(a) and N-H<sub>2</sub><sup>\*</sup>(b) complexes, respectively.

Finally, the Ga-H<sub>BC</sub>-N-H<sub>BC</sub>-Ga<sup>+2</sup> complex shown in Fig. 2(e) (also referred to as N-2H<sub>BC</sub><sup>+2</sup>) represents a novel charged dihydrogen complex involving two H<sub>BC</sub><sup>+</sup> ions both bonded to the N atom. In this case, each H<sup>+</sup> ion is aligned with its neighboring N and Ga atoms, thus leading to a C<sub>2v</sub> symmetry for the complex quite different from the C<sub>∞v</sub> symmetry of the above H<sub>2</sub><sup>\*</sup> dihydrogen complexes. An As-2H<sub>BC</sub><sup>+2</sup> complex with a C<sub>2v</sub> symmetry similar to that of the N-2H<sub>BC</sub><sup>+2</sup> complex is not stable in GaAs. In the N-2H<sub>BC</sub><sup>+2</sup> complex, the N-H<sub>BC</sub><sup>+</sup> bond-lengths are equal to the N-H bond length in the N-H<sub>BC</sub><sup>+</sup>(-Ga) complex. The charge states +1, 0, and -1 of this complex have been also investigated. The corresponding geometries (not reported in Table II) differ from that of the complex with charge +2 mainly for the atomic displacements of the Ga atoms and the Ga-H atomic distances. In detail, the Ga displacements and the Ga-H distances decrease from 0.64 Å to 0.28 Å and from 2.43 Å to 2.00 Å, respectively, on going from +2 to -1 charge of the complex, in agreement with the local relaxations found in the case of the monohydrogen N-H<sub>BC</sub><sup>+</sup>(-Ga) complex (see Table I).

### C. Formation energies of N-H complexes in GaAsN

The formation energies per H atom of the most interesting monohydrogen and dihydrogen complexes for different values of  $\mu_e$  are given in Table III.<sup>21</sup> Formation energies of H<sub>2</sub> molecules in GaAsN and H<sub>BC</sub><sup>+</sup>, H<sub>2</sub><sup>\*</sup>, and H<sub>2</sub> molecules in GaAs are also reported in the same table.<sup>22</sup> In the case of the H<sub>2</sub> molecules, H<sub>2</sub>(Ga) [H<sub>2</sub>(N)] indicates a molecule located close to a Td site that has Ga (N and As) atoms as nearest neighbors.

The present results indicate that the formation of strong N-H bonds stabilize both the H<sub>BC</sub><sup>+</sup> and H<sub>2</sub><sup>\*</sup> complexes with respect to the case of GaAs. In fact, in GaAs, the H<sub>2</sub> molecule is the most stable species for almost all the  $\mu_e$  values in the energy gap. On the other hand, in GaAsN, the N-H<sub>2</sub><sup>\*</sup> complexes and the N-H<sub>BC</sub> complexes (in the various charge states) are always more stable than the H<sub>2</sub> molecules. The stabilizing effect produced by the formation of strong N-H bonds is also shown by the existence of the N-2H<sub>BC</sub><sup>+2</sup> complex. In fact, as previously noted, a corresponding As-2H<sub>BC</sub><sup>+2</sup> complex is not stable in GaAs.

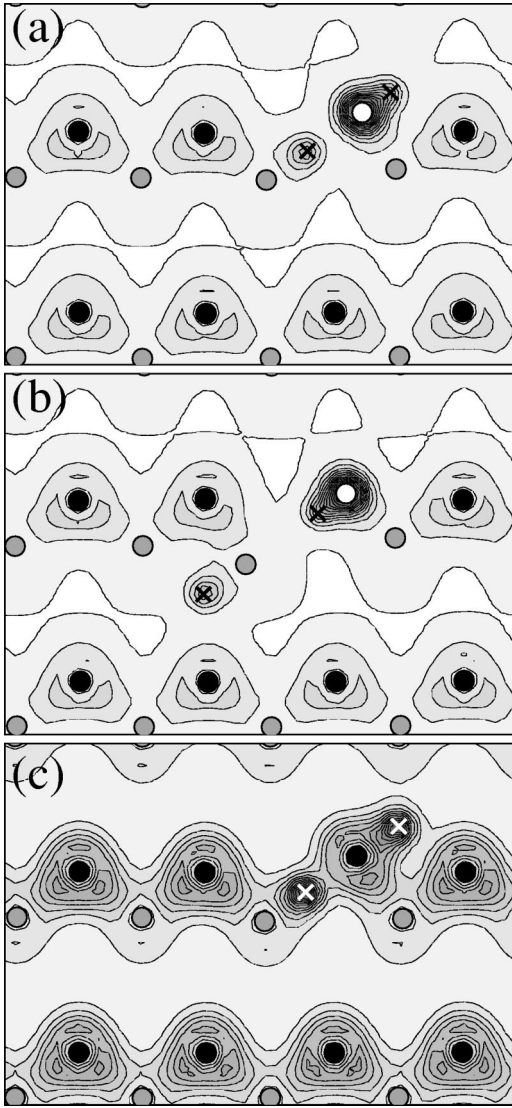


FIG. 4. Contour plots in the (110) plane of the total (valence) charge density corresponding to (a) the  $\text{N-H}_2^*(\text{a})$  complex, (b) the  $\text{N-H}_2^*(\text{b})$  complex, and (c) the  $\text{Ga-H}_{\text{BC}}-\text{As-H}_{\text{AB}}$  complex. The As, Ga, and N atoms are indicated by black, gray, and white full dots, respectively. Small black or white crosses represent the H atoms.

The results in Table III also indicate that  $p$ -type and  $n$ -type doping have significant effects on the formation of the N-H complexes. When the Fermi level is close to the valence band maximum (VBM), the  $\text{N-H}_{\text{BC}}^+$  complex is the most favored one. The  $\text{N-2H}_{\text{BC}}^{+2}$  and  $(\text{Ga})\text{-N-H}_{\text{AB}}^+$  complexes have also very small formation energies. In semi-intrinsic GaAsN, the  $\text{N-H}_{\text{BC}}^+$  and  $\text{N-H}_2^*$  complexes should coexist, whereas the  $\text{N-H}_2^*$  and  $\text{N-H}_{\text{BC}}^-$  complexes should prevail when the Fermi level is close to the conduction band minimum (CBM).

The above discussion gives a simplified description of the effects of doping on the formation of monohydrogen and dihydrogen complexes. In fact, it has to be taken into account that hydrogenation can change the position of the Fermi level in a given semiconductor because H passivates the shallow impurities. Thus, in  $p$ -type GaAsN, the  $\text{N-H}_{\text{BC}}^+$ ,  $\text{N-H}_{\text{AB}}^+$ , and  $\text{N-2H}_{\text{BC}}^{+2}$  complexes are favored at the beginning

TABLE III. Formation energies per H atom (in eV) of H complexes and molecules in  $\text{GaAs}_{0.97}\text{N}_{0.03}$  calculated for Fermi energy ( $\mu_e$ ) values equal to 0 (top of the valence band),  $E_g/2$ , and  $E_g$ , where  $E_g$  is the experimental GaAs energy gap (1.52 eV). Formation energies per H atom of several H complexes and molecules in GaAs are given in the last three rows of the table.

Complex	0	$E_g/2$	$E_g$
$[\text{N-H}_{\text{BC}}^+(\text{-Ga})]$	-1.01	-0.25	0.51
$[\text{N-H}_{\text{BC}}^0(\text{-Ga})]$	0.07	0.07	-0.07
$[\text{N-H}_{\text{BC}}^-(\text{-Ga})]$	1.31	0.55	-0.21
$[(\text{Ga})\text{-N-H}_{\text{AB}}^+]$	-0.85	-0.09	0.67
$[(\text{Ga})\text{-N-H}_{\text{AB}}^0]$	0.39	0.39	0.39
$[(\text{Ga})\text{-N-H}_{\text{AB}}^-]$	1.43	0.67	-0.09
$[\text{N-H}_2^*(\text{a})]$	-0.28	-0.28	-0.28
$[\text{N-H}_2^*(\text{a})^{-1}]$	0.81	0.43	0.05
$[\text{N-H}_2^*(\text{b})]$	-0.21	-0.21	-0.21
$[\text{N-2H}_{\text{BC}}^{+2}]$	-0.94	-0.18	0.58
$[\text{N-2H}_{\text{BC}}^{+1}]$	-0.48	-0.10	0.28
$[\text{N-2H}_{\text{BC}}^0]$	-0.03	-0.03	-0.03
$[\text{N-2H}_{\text{BC}}^{-1}]$	0.92	0.54	0.16
$[\text{H}_2(\text{N})]$	0.41	0.41	0.41
$[\text{H}_2(\text{Ga})]$	0.23	0.23	0.23
$[\text{H}_{\text{BC}}^+]$	0.05	0.81	1.57
$[\text{H}_2^*]$	0.56	0.56	0.56
$[\text{H}_2(\text{Ga})]$	0.20	0.20	0.20

of hydrogenation. Then, the Fermi level raises due to the H passivation of the shallow acceptors and the  $\text{N-H}_2^*$  complexes start to form. When the Fermi level reaches the midgap, the  $\text{N-H}_{\text{BC}}^+$  and the  $\text{N-H}_2^*$  complexes are the most favored complexes. The  $\text{N-H}_{\text{AB}}^+$ , and  $\text{N-2H}_{\text{BC}}^{+2}$  complexes previously formed are likely still present. Thus, one should expect that all the above four complexes can be observed in hydrogenated  $p$ -type GaAsN. On the other hand, interestingly, not all of the above four complexes should be formed in hydrogenated  $n$ -type GaAsN. Preliminarily, it should be observed that, for a Fermi level close to the CBM of GaAsN, the  $\text{N-H}_2^*(\text{a})^{-1}$  and the  $\text{N-2H}_{\text{BC}}^{-1}$  complexes should not be formed, although they have small formation energies. This will be clarified in the next section, where it will be shown that the  $\epsilon^{0/-}$  transition energies corresponding to the above two complexes are higher than the GaAs (and GaAsN) CBM. Thus, the neutral  $\text{N-H}_2^*$  and the  $\text{N-H}_{\text{BC}}^{-1}$  complexes start to form in  $n$ -type GaAsN. The formation of the  $\text{N-H}_{\text{AB}}^+$  and  $\text{N-2H}_{\text{BC}}^0$  complexes is instead uncertain due to their higher formation energies. Then, hydrogen passivates the shallow donors, thus lowering the Fermi level. When  $\mu_e$  is close to midgap, the  $\text{N-H}_2^*$ , the  $\text{N-H}_{\text{BC}}^{+1}$  complexes should be present, while the presence of  $\text{N-H}_{\text{AB}}^+$  and  $\text{N-2H}_{\text{BC}}^0$  complexes remains uncertain. The above results have significant consequences. (i) After hydrogenation, the Fermi level is located close to the midgap independent on the initial doping conditions. This implies that the  $\text{N-H}_2^*$  complexes are formed both in  $p$ - and  $n$ -type GaAsN. In turn, this is an important result,

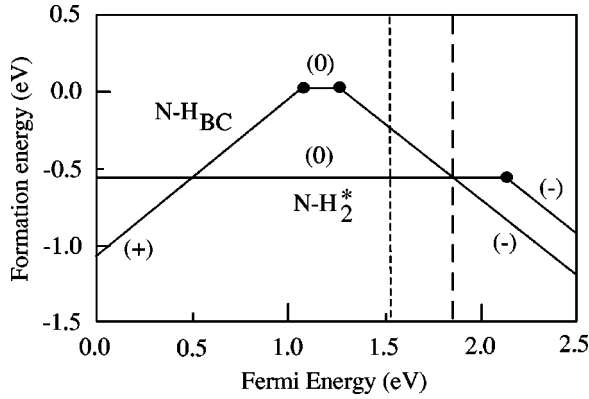


FIG. 5. Formation energy as a function of the Fermi energy  $\mu_e$  for the  $\text{N-H}_{\text{BC}}$  and  $\text{N-H}_2^*$  complexes in  $\text{GaAs}_{0.97}\text{N}_{0.03}$ . The vertical short-dashed and long-dashed lines correspond to the  $\epsilon^{0^-}[\text{N}]$  and  $\epsilon^{0^-}[\text{GaAs}]$  values, respectively, namely to the energy gaps of  $\text{GaAs}_{0.97}\text{N}_{0.03}$  and GaAs (1.51 and 1.85 eV, respectively). The line segments represent the charge states of the complexes and the dots indicate the transition energies.

because the  $\text{N-H}_2^*$  complexes are the main responsible of the N passivation, as will be clarified in the following section. (ii) Different hydrogen LVM's should be observed in the case of  $p$ -type and  $n$ -type GaAsN.

#### D. Transition energies for the N-H complexes and N passivation in GaAsN

The hydrogen neutralization of the nitrogen effects on the GaAs energy gap will be discussed here. The  $\epsilon^{0^-}[\text{GaAs}]$  value calculated for pure GaAs (i.e., the present estimate of the GaAs energy gap) is 1.85 eV, 22% higher than the experimental value (1.52 eV). An  $\epsilon^{+/0}$  value of 1.84 eV has been also estimated here for the electronic level induced in the energy gap by a Si donor ( $\text{Si}_{\text{Ga}}$ ) in GaAs. In agreement with the shallow character of this dopant, the  $\epsilon^{+/0}[\text{Si}_{\text{Ga}}]$  value is close to the  $\epsilon^{0^-}[\text{GaAs}]$  value, thus indicating a good consistency of the present approach. The  $\epsilon^{0^-}[\text{N}]$  value calculated for an isolated N atom in GaAs is 1.51 eV from the top of the valence band. This value is assumed as the energy gap of the  $\text{GaAs}_{0.97}\text{N}_{0.03}$  alloy, thus corresponding to a reduction of 340 meV of the calculated GaAs energy gap, close to the experimental value of 400 meV.<sup>23</sup> Let us now consider the N passivation in the case of  $p$ -type GaAsN. In this case, it has been shown in the previous section that the most stable  $\text{N-H}_{\text{BC}}^+$  complex, the  $\text{N-H}_{\text{AB}}^+$ , and the  $\text{N-2H}_{\text{BC}}^{+2}$  complexes start to form at the beginning of hydrogenation. Then, the Fermi level raises and the  $\text{N-H}_2^*$  complexes are formed. The formation energies of the  $\text{N-H}_{\text{BC}}$  and  $\text{N-H}_2^*(a)$  complexes as a function of the Fermi level are reported in Fig. 5. In this figure, the crossing points of the formation energies corresponding to different charge-states of the complexes permit to estimate the transition energy values. Figure 5 shows that the  $\epsilon^{+/0}[\text{N-H}_{\text{BC}}]$  is about 0.4 eV lower than the energy gap estimated for the  $\text{GaAs}_{0.97}\text{N}_{0.03}$  alloy. The  $\epsilon^{0^-}[\text{N-H}_{\text{BC}}]$  is about 0.2 eV higher than the  $\epsilon^{+/0}[\text{N-H}_{\text{BC}}]$  value and still lower than the GaAsN energy gap. Similar

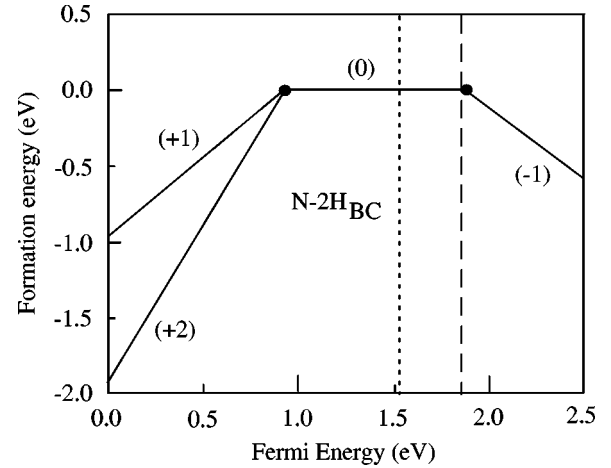


FIG. 6. Formation energy as a function of the Fermi energy  $\mu_e$  for the  $\text{N-2H}_{\text{BC}}$  complexes in  $\text{GaAs}_{0.97}\text{N}_{0.03}$ . The vertical short-dashed and long-dashed lines correspond to the  $\epsilon^{0^-}[\text{N}]$  and  $\epsilon^{0^-}[\text{GaAs}]$  values, respectively, namely to the energy gaps of  $\text{GaAs}_{0.97}\text{N}_{0.03}$  and GaAs (1.51 and 1.85 eV, respectively). The line segments represent the charge states of the complexes and the dots indicate the transition energies.

results have been achieved in the case of the  $\text{N-H}_{\text{AB}}^+$  complex. For what concerns the  $\text{N-H}_2^*(a)$  complex, the  $\epsilon^{+/0}[\text{N-H}_2^*(a)]$  value (not shown in Fig. 5) is close to the VBM of GaAsN. The  $\epsilon^{0^-}[\text{N-H}_2^*(a)]$  value is instead about 0.3 eV higher than the energy gap estimated for pure GaAs. A similar result is obtained in the case of the  $\text{N-H}_2^*(b)$  complex. Although the calculated  $\epsilon^{n/n+1}$  values are affected by the well-known LDA band-gap error, the qualitative result is clear: the effects of N in GaAs can be neutralized by the formation of the  $\text{N-H}_2^*$  complexes, while monohydrogen complexes do not restore the GaAs gap.

A similar analysis of the transition energies has been performed in the case of the  $\text{N-2H}_{\text{BC}}$  complexes, see Fig. 6. The  $\epsilon^{+2/+1}[\text{N-2H}_{\text{BC}}]$  and  $\epsilon^{+/0}[\text{N-2H}_{\text{BC}}]$  transition energies show that the formation of the complexes with charge +2 and +1 does not lead to the N passivation. The GaAs energy gap could be restored instead by the formation of the neutral  $\text{N-2H}_{\text{BC}}^0$  complex as shown by a value of 1.91 eV estimated for the  $\epsilon^{0^-}[\text{N-2H}_{\text{BC}}]$  transition energy.

On the ground of the above results, it can be concluded that, in the case of  $p$ -type GaAsN, the  $\text{N-H}_2^*$  complexes are the main responsible of N passivation. Some contribution to the passivation process can be given by the  $\text{N-2H}_{\text{BC}}$  complexes. In the case of  $n$ -type GaAsN, the  $\text{N-2H}_{\text{BC}}$  complexes should not be formed. The N passivation is achieved therefore only through the formation of the  $\text{N-H}_2^*$  complexes.

A model can be proposed now to explain why the N neutralization is not achieved by forming the monohydrogen  $\text{N-H}_{\text{BC}}^+$  complexes and realized through the formation of the  $\text{N-H}_2^*$  complexes. This model is based on an analysis of (i) the bonding or antibonding character of the electronic states induced by the  $\text{N-H}_{\text{BC}}^+$  and  $\text{N-H}_2^*$  complexes and (ii) the local lattice relaxations occurring in the  $\text{N-H}_{\text{BC}}^+$  complexes. Contour plots in the (110) plane of the charge densities  $|\Psi_{n,0}|^2$

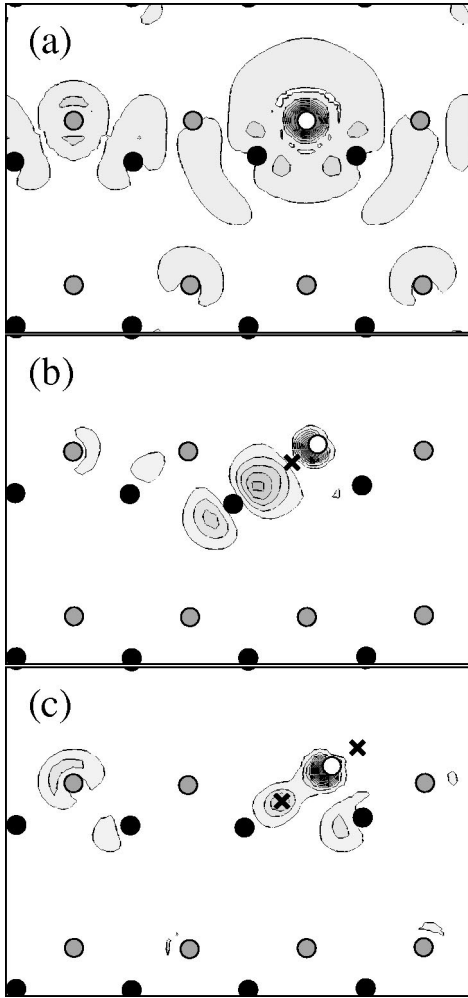


FIG. 7. Contour plots in the (110) plane of the charge density  $|\Psi_{n,0}|^2$  corresponding to the lowest unoccupied molecular orbital (LUMO) of (a) an isolated N atom, (b) the  $\text{N-H}_{\text{BC}}^+$  complex, and (c) the  $\text{N-H}_2^*(\text{a})$  complex, in  $\text{GaAs}_{0.97}\text{N}_{0.03}$ . The Ga, As and N atoms are indicated by black, gray, and white full dots, respectively. Small crosses represent the H atoms.

corresponding to the lowest *unoccupied* molecular orbitals (LUMO) induced by an isolated N atom and its H complexes are shown in Fig. 7. The LUMO of the isolated N (i.e., the conduction band minimum of GaAsN) is characterized by a strong localization of the electronic charge on the N atom, see Fig. 7(a). The formation of the  $\text{N-H}_{\text{BC}}^+$  complex gives rise to an occupied level in valence band corresponding to the formation of a strong N-H bond and to the LUMO of Fig. 7(b). Three main features characterize the latter state: (a) the electronic charge is still strongly localized on the N atom as in the case of isolated N, although polarized toward the  $\text{H}^+$  ion, (b) the charge distribution of Fig. 7(b) clearly shows the existence of a dangling bond of the Ga neighboring the H ion that points toward the H itself, (c) the LUMO of Fig. 7(b) has not an antibonding character. It can induce instead a weak bonding  $\text{Ga-H}_{\text{BC}}$  interaction. In detail, the point (a) can be explained in terms of a  $\text{H}^+$  ion taking the place of the Ga atom no longer bonded to the N atom. The N atom forms indeed a stable N-H bond and still keeps its five electrons to

TABLE IV. Stretching frequency values (in  $\text{cm}^{-1}$ ) calculated for the H local vibration modes in several N-H complexes in GaAsN (left column) and InGaAsN (right column).

Complex	Bond	$\nu_{\text{GaAsN}}$	$\nu_{\text{InGaAsN}}$
$[\text{N-H}_{\text{BC}}^+(\text{-Ga})]$	$\text{N-H}_{\text{BC}}$	3172	3170
$[(\text{Ga-})\text{N-H}_{\text{AB}}^+]$	$\text{N-H}_{\text{AB}}$	3118	3102
$[\text{N-H}_2^*(\text{a})]$	$\text{Ga-H}_{\text{BC}}$	2025	1794
$[\text{N-H}_2^*(\text{a})]$	$\text{N-H}_{\text{AB}}$	3035	3086
$[\text{N-H}_2^*(\text{b})]$	$\text{Ga-H}_{\text{AB}}$	1708	
$[\text{N-H}_2^*(\text{b})]$	$\text{N-H}_{\text{BC}}$	3131	
$[\text{N-2H}_{\text{BC}}^{+2}]$	$\text{N-H}_{\text{BC}}$	3210	3198
$[\text{N-2H}_{\text{BC}}^{+2}]$	$\text{N-H}_{\text{BC}}$	3100	3095

form four chemical bonds, i.e., three N electrons are involved in three Ga-N bonds and the remaining two electrons bind the  $\text{H}_{\text{BC}}^+$  ion instead of the fourth Ga atom. Thus, the  $\text{H}^+$  insertion in the Ga-N bond does not affect the main characteristic of the original nitrogen LUMO, that is, the strong charge localization on N. On the other hand, the fact that the Ga dangling bond can induce a  $\text{Ga-H}_{\text{BC}}$  bonding interaction, points (b) and (c) above, is supported by the previous discussion of the atomic relaxations occurring in the  $\text{N-H}_{\text{BC}}$  complexes, see Sec. III A. Those results show indeed that, when occupied by one or two electrons, the LUMO of Fig. 7(b) induces a progressive reduction of the  $\text{Ga-H}_{\text{BC}}$  distance as shown by the geometries of the  $\text{N-H}_{\text{BC}}^+$ ,  $\text{N-H}_{\text{BC}}^0$ , and  $\text{N-H}_{\text{BC}}^-$  complexes, see Table I. The characteristics of the LUMO of the  $\text{N-H}_{\text{BC}}^+$  complex (i.e., its similarities with the LUMO of the isolated N and the absence of any antibonding character) account for the fact that this state is not higher in energy than the LUMO of the isolated N as well as for the closeness of  $\epsilon^{0/-}[\text{N}]$  and  $\epsilon^{+/0}[\text{N-H}_{\text{BC}}]$  values. The formation of a mono-hydrogen complex cannot lead therefore to the N passivation. On the other hand, in the  $\text{N-H}_2^*(\text{a})$  complex, two N electrons and the two electrons of the H atoms are involved in the formation of the Ga-H and N-H bonds. The occupied electronic levels corresponding to these stable bonds are located in and close to the top of the valence band. The latter bonding state has its antibonding counterpart in the LUMO shown in Fig. 7(c). In this state, the charge is still localized on the N atom but polarized towards the H atom, that is, towards the atom bonded to the Ga atom. Furthermore, there is some charge localization between the same two non bonded H and N atoms. This charge localization reveals a strong antibonding character of this electronic state, that accounts for an  $\epsilon^{0/-}[\text{N-H}_2^*(\text{a})]$  higher than  $\epsilon^{0/-}[\text{N}]$  and  $\epsilon^{+/0}[\text{N-H}_{\text{BC}}]$  and also higher than the value estimated for the bottom of the GaAs conduction band. Similar results are obtained for the  $\text{N-H}_2^*(\text{b})$  complex. The above model and the calculated transition energies provide therefore a firm theoretical framework for understanding why the hydrogen passivation of N in GaAsN is not achieved by forming mono-hydrogen complexes and realized through the formation of  $\text{N-H}_2^*$  complexes.



TABLE V. Atomic distances, atomic displacements with respect to ideal positions ( $\Delta X$  values), and total energy values of several mono-hydrogen complexes in InGaAsN. Positive (negative)  $\Delta X$  values indicate an outward (inward) atomic displacement with respect to the chemical bond. Total energy values are relative to the energy of the most stable complex (for each H species) that is taken equal to zero. Distances are given in angstroms, total energies in eV. In the case of the As-H<sub>BC</sub><sup>+</sup>-Ga complex, the  $\Delta$ As and As- $X$  values are reported in the  $\Delta$ N and N- $X$  columns ( $X$  = Ga, H), respectively.

Complex	N-H	Ga-H	Ga-N	$\Delta$ Ga	$\Delta$ N	$E$
[N-H <sub>BC</sub> <sup>+</sup> (-Ga)]	1.05	2.54	3.59	0.67	0.51	0.00
[(Ga-)N-H <sub>AB</sub> <sup>+</sup> ]	1.06	4.87	3.81	0.53	0.83	0.70
[As-H <sub>BC</sub> <sup>+</sup> -Ga]	1.56	1.88	3.29	0.54	0.34	
[N-H <sub>BC</sub> <sup>0</sup> (-Ga)]	1.08	2.17	3.25	0.29	0.55	
[N-H <sub>BC</sub> <sup>-</sup> (-Ga)]	1.08	2.00	3.08	0.08	0.73	

Finally, in a previous paper,<sup>6</sup> it has been suggested that monoatomic hydrogen can exist only in the donor charge state in GaAsN. In that study, the calculated transition energy level  $\epsilon^{+/-}$ [N-H<sub>BC</sub>] results indeed to be located about 0.03 eV above the CBM of GaAsN. We cannot confirm that result because our findings show that the  $\epsilon^{+/0}$ [N-H<sub>BC</sub>] and  $\epsilon^{0/-}$ [N-H<sub>BC</sub>] transition energy levels are both below the CBM of GaAsN. On one hand, our estimates of transition energy levels and energy gaps are less accurate than those calculated in the study cited above and could not reveal the small difference between the  $\epsilon^{+/-}$ [N-H<sub>BC</sub>] and the CBM values reported in that study. On the other hand, the very small difference between those two values would need further experimental investigation in order to confirm the donor behavior of H in GaAsN. In this concern, our previous considerations on the N-H complexes formed in *n*-type GaAsN could be useful. On the ground of the discussion made in Sec. III C, the N-H<sub>BC</sub><sup>-1</sup> complex should be formed indeed only if  $\epsilon^{0/-}$ [N-H<sub>BC</sub>] is lower than the CBM of GaAsN. It is also worth noticing that the donor behavior of H suggested in the case of GaAsN should be more marked in InGaAsN due to the smaller energy gap of this alloy. In InGaAsN, present results confirm that monoatomic hydrogen can exist only in the donor charge state, as will be discussed in Sec. III F.

### E. Hydrogen local vibrational modes in GaAsN

Present results indicate that a number of N-H complexes can be formed in GaAsN. Moreover, they suggest that different complexes should be formed after hydrogenation of *p*-type and *n*-type GaAsN. Theoretical and experimental work is therefore in progress to achieve a detailed description of the quite complicated vibrational properties of the N-H complexes in GaAsN. Some preliminary results are given here, see Table IV, that should be confirmed by infrared spectroscopy experiments. These results show that the stretching frequencies corresponding to the N-H bonds are in the range of 3035–3210 cm<sup>-1</sup>. Although present results are characterized by an error bar of about 100 cm<sup>-1</sup>,<sup>24</sup> they give useful informations to distinguish between the different complexes. As an example, the results in Table IV show that the N-H<sub>BC</sub> stretching frequencies are always greater than the N-H<sub>AB</sub> ones, both in monohydrogen and dihydrogen complexes. This result and the different stretching frequencies of the Ga-H<sub>BC</sub> and Ga-H<sub>AB</sub> bonds in the N-H<sub>2</sub><sup>\*</sup>-like complexes should permit to distinguish between the N-H<sub>2</sub><sup>\*</sup>(a) and the N-H<sub>2</sub><sup>\*</sup>(b) complexes. Moreover, a significant result is achieved in the case of the N-2H<sub>BC</sub><sup>+2</sup> complex, that results to be the only N-H complex giving rise to two close N-H stretching frequencies. These frequencies represent a fingerprint of the complex that could be observed experimentally by isotopic shifts induced by the use of deuterium in place of hydrogen.

### F. Hydrogen complexes in InGaAsN

Monohydrogen and dihydrogen complexes such as those shown in Figs. 1 and 2 have been investigated in the case of InGaAsN. In addition, in this alloy, we have also investigated complexes where an In atom is involved in place of a Ga atom, e.g., the N-H<sub>BC</sub><sup>+</sup>(-In) complex has been considered in place of the N-H<sub>BC</sub><sup>+</sup>(-Ga) complex of Fig. 1(a). All the complexes involving an In atom in place of the Ga atom are high in energy. Thus, only the former complexes will be discussed in the following. The geometries of the most stable monohydrogen complexes are given in Table V together with the geometry of the As-H<sub>BC</sub><sup>+</sup>-Ga complex in InGaAs. The geometries of some dihydrogen complexes are given in Table VI.

TABLE VI. Atomic distances, atomic displacements with respect to ideal positions ( $\Delta X$  values), and total energy values for several di-hydrogen complexes in InGaAsN. Positive (negative)  $\Delta X$  values indicate an outward (inward) atomic displacement with respect to the chemical bond. Total energy values are relative to the energy of the most stable complex that is taken equal to zero. Distances are given in angstroms, total energies in eV. In the case of the Ga-H<sub>1(BC)}</sub>-As-H<sub>2(AB)}</sub> complex, the  $\Delta$ As and As- $X$  values are reported in the  $\Delta$ N and N- $X$  columns ( $X$  = Ga, H), respectively.

Complex	N-H <sub>1</sub>	N-H <sub>2</sub>	Ga-H <sub>1</sub>	Ga-H <sub>2</sub>	Ga-N	$\Delta$ N	$\Delta$ Ga	$E$
[Ga-H <sub>1(BC)}</sub> -N-H <sub>2(AB)}</sub> (a)	2.26	1.06	1.58	4.72	3.67	1.10	0.16	0.0
[H <sub>1(AB)}</sub> -Ga-H <sub>2(BC)}</sub> -N](b)	5.49	1.06	1.60	2.83	3.89	0.49	1.00	0.18
[H <sub>1(AB)}</sub> -Ga-N-H <sub>2(AB)}</sub> (c)	5.92	1.06	1.66	5.36	4.31	0.91	0.98	0.51
[Ga-H <sub>1(BC)}</sub> -As-H <sub>2(AB)}</sub> ]	2.03	1.57	1.55	5.11	3.54	0.90	0.21	
[Ga-H <sub>1(BC)}</sub> -N-H <sub>2(BC)}</sub> -Ga <sup>+2</sup> ]	1.05	1.05	2.49		3.52	0.63	0.66	

TABLE VII. Formation energies per H atom (in eV) of H complexes and molecules in  $\text{InGaAs}_{0.97}\text{N}_{0.03}$  calculated for Fermi energy ( $\mu_e$ ) values equal to 0 (top of the valence band),  $E_g/2$ , and  $E_g$ , where  $E_g$  is the estimated InGaAs energy gap (1.21 eV). Formation energies per H atom of H complexes in InGaAs are given in the last two rows of the table.

Complex	0	$E_g/2$	$E_g$
$[\text{N-H}_{\text{BC}}^+(-\text{Ga})]$	-1.03	-0.43	0.18
$[\text{N-H}_{\text{BC}}^0(-\text{Ga})]$	-0.17	-0.17	-0.17
$[\text{N-H}_{\text{BC}}^-(-\text{Ga})]$	0.86	0.26	-0.35
$[(\text{Ga})\text{N-H}_{\text{AB}}^+]$	-0.47	0.13	0.74
$[\text{N-H}_2^*(\text{a})]$	-0.45	-0.45	-0.45
$[\text{N-H}_2^*(\text{a})^{-1}]$	0.50	-0.10	-0.71
$[\text{N-H}_2^*(\text{b})]$	-0.35	-0.35	-0.35
$[\text{N-2H}_{\text{BC}}^{+2}]$	-0.78	0.43	1.64
$[\text{H}_2(\text{Ga})]$	0.20	0.20	0.20
$[\text{H}_{\text{BC}}^+]$	0.20	0.80	1.41
$[\text{H}_2^*]$	0.44	0.44	0.44

The formation energies of the most interesting monohydrogen and dihydrogen complexes are given in Table VII.

The results achieved for InGaAsN almost parallel those found in the case of GaAsN. In the case of the monohydrogen complexes, the BC site close to the N atom is, once more, the most stable site for all the three  $\text{H}^+$ ,  $\text{H}^0$ , and  $\text{H}^-$  species. The geometries of the monohydrogen and dihydrogen complexes indicate that strong N-H bonds are formed in both complexes. The formation energies reported in Table VII show that the  $\text{N-H}_{\text{BC}}$  and  $\text{N-H}_2^*$  complexes are more stable than the  $\text{H}_2$  molecules. Even the existence of the  $\text{N-2H}_{\text{BC}}$  complexes is confirmed in the case of InGaAsN. All these results indicate therefore that the presence of the bigger In atoms and the disorder induced by the random distribution of two different cations in the lattice do not affect the main properties of the N-H complexes. Moreover, they further support the suggestion that the energetics of those complexes is dominated by the formation of strong N-H bonds.

Present results also indicate that the  $\text{N-H}_{\text{BC}}^+$  and  $\text{N-2H}_{\text{BC}}^{+2}$  complexes are favored by  $p$ -type doping as in the case of GaAsN. The transition energy values for the  $\text{N-H}_{\text{BC}}^+$  and  $\text{N-H}_2^*(\text{a})$  complexes are given in Fig. 8, together with the estimated energy gap of the  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$  alloy and the shallow level corresponding to the Si donor. The achieved results show that only the formation of the  $\text{N-H}_2^*(\text{a})$  complex permits us to restore the InGaAs energy gap. Thus, the model proposed to explain the N passivation in the case of GaAsN still holds for InGaAsN. All the previous results show that the properties of the N-H complexes are quite similar in GaAsN and InGaAsN.

On the other hand, as anticipated before, the transition energies estimated here for the N-H complexes in InGaAsN reveals a donor behavior of H at variance with the case of GaAsN. The transition energy values corresponding to different charge states of the  $\text{N-H}_{\text{BC}}$  complex are shown in Fig. 8. The  $\epsilon^{+/0}$ ,  $\epsilon^{0/-}$ , and  $\epsilon^{+/-}$  values for that complex are almost coincident and located above the value estimated for

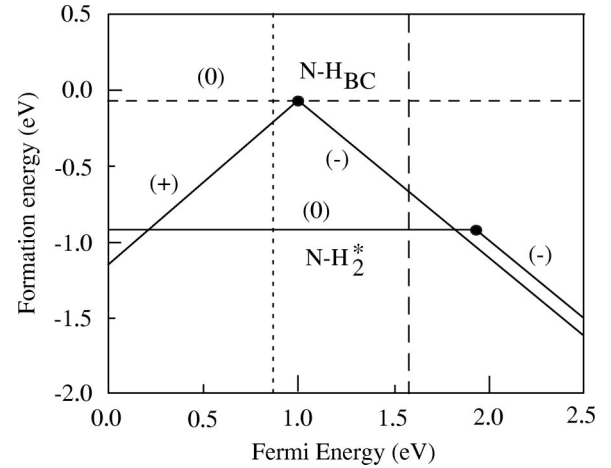


FIG. 8. Formation energy as a function of the Fermi energy  $\mu_e$  for the  $\text{N-H}_{\text{BC}}$  and  $\text{N-H}_2^*$  complexes in  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$ . The vertical short-dashed and long-dashed lines correspond to the  $\epsilon^{0/-}[\text{InGaAsN}]$  and  $\epsilon^{0/-}[\text{InGaAs}]$  values, respectively, namely to the energy gaps of  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}_{0.97}\text{N}_{0.03}$  and  $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$  (0.82 and 1.62 eV, respectively). The line segments represent the charge states of the complexes and the dots indicate the transition energies.

the InGaAsN CBM. This result seems to confirm that monoatomic hydrogen can exist only in the donor charge state in this alloy, as suggested in a previous paper.<sup>6</sup> This donor behavior of H implies that in  $n$ -doped InGaAsN only the  $\text{N-H}_2^*$  complexes should be formed, at variance with the case of GaAsN.

Finally, preliminary stretching frequency values calculated for N-H complexes in InGaAsN are given in Table IV. The discussion made in Sec. III E about the vibrational properties of the N-H complexes in GaAsN can be extended to the case of InGaAsN.

#### IV. CONCLUSIONS

In conclusion, previous investigations on N-H complexes in GaAsN have been extended here to dihydrogen complex configurations different from the  $\text{H}_2^*$  configurations and to N-H complexes in InGaAsN. Moreover, the structure, the formation energies, the chemical bonding and the electronic properties of the old and new N-H complexes have been analyzed in detail in order to achieve a sound model for the N passivation. The existence of a novel dihydrogen complex is predicted that is characterized by a  $C_{2v}$  symmetry different from the  $C_{\infty v}$  symmetry of the  $\text{H}_2^*$  dihydrogen complexes investigated in previous studies. This complex is quite stable and can give rise to infrared vibrational modes that should be revealed by infrared spectroscopy measurements. It can also contribute to the nitrogen passivation. However, present results confirm that the  $\text{N-H}_2^*$  complexes are the main responsible of the N passivation. A model is proposed for the N passivation by hydrogen that is firmly founded on the bonding or antibonding characters of the electronic states induced by the monohydrogen and dihydrogen complexes and on a careful analysis of the geometries of the monohydrogen complexes. This model explains why the N passivation is not achieved in the case of monohydrogen complexes and real-

ized by N-H<sub>2</sub><sup>\*</sup> dihydrogen complexes. Present results also show that different N-H complexes and different vibrational spectra should be observed in hydrogenated *p*-type and *n*-type N-containing alloys.

Finally, the results obtained for the N-H complexes in InGaAsN parallel those achieved in GaAsN, thus indicating that the energetics of these complexes is dominated by the formation of strong N-H bonds.

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<sup>1</sup>See, e. g., *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Vol. 34 of *Semiconductors and Semimetals*, (Academic, New York, 1991).

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<sup>21</sup>A correction term has been applied to the formation energies of Table III, as described in Ref. 11. This term was applied to the neutral charge state of a complex in Ref. 7 and to the positive charge state here. This and a better convergence of present calculations account for some differences between the results presented here and in Ref. 7.

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<sup>24</sup>A stretching frequency of 3410 cm<sup>-1</sup> has been calculated for the N-H bond in the NH<sub>3</sub> molecule against the experimental values of 3414 cm<sup>-1</sup> and 3336 cm<sup>-1</sup>.