

Atomic and molecular hydrogen in gallium arsenide: A theoretical study

L. Pavese

Dipartimento di Fisica, Università di Trento, I-38050 Povo (Trento), Italy

P. Giannozzi

Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56100 Pisa, Italy

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We present first-principles calculations of the properties of atomic and molecular hydrogen in pure bulk GaAs. Our results indicate that H penetrates into GaAs in atomic form. Inside GaAs, atomic H tends to form H₂ molecules in tetrahedral sites, which are deep energy wells for H₂. The H₂⁺ defect, formed by one H in a bond-center site and one H in an adjacent tetrahedral position, has higher energy than H₂ but lower-energy barriers for diffusion. Isolated H could be present as a metastable species. We compute the stable charge state of isolated H as a function of the Fermi energy. Our results suggest that H behaves as a negative-*U* defect. As a consequence, isolated H is expected to be present only as a charged species (positively charged in *p*-doped samples, negatively charged in undoped and *n*-doped samples). Our conclusions are compared with experimental results and with the results of calculations for H in other semiconductors. The main features of H in GaAs are quite similar to what has been found in Si.

I. INTRODUCTION

GaAs and related compounds are corner-stone materials in high-speed microelectronic and optoelectronic technology. Modern epitaxial-growth techniques have succeeded in producing high-quality crystals, with very low defect density. Nevertheless the increase in device complexity and the decrease in device dimensions require crystals of higher and higher purity. Device engineers are asking for post-growth techniques to improve or change sample properties and to control the properties of impurities and defects. Intentional hydrogen exposure could be such a technique. Hydrogen diffuses quite easily in semiconductors via interstitial sites and binds to impurity centers (both shallow and deep impurities, lattice defects, dangling bonds). The consequent reduction of the electrical activity of shallow levels (*passivation*) through the formation of neutral H-impurity complexes has a special interest in view of potential technological applications.

Much theoretical and experimental work has been done in recent years on H in GaAs and other elemental or compound semiconductors.¹ While the general features of passivation and formation of H-impurity complexes are quite well understood, less is known, both on the theory side and from experiments, about H diffusion, the charge state of the diffusing species, and the diffusion paths. Indiffused elemental profile [as measured by secondary ion mass spectroscopy (SIMS)] and electrical depth profile [capacitance-voltage (CV) measurements] do not correlate closely. This suggests that the diffusion dynamics is complicated, with H trapping to defects, and molecule formation.

The most complete theoretical results have been ob-

tained for H in Si with first-principles local-density-approximation (LDA) supercell calculations.^{2,3} The equilibrium sites for isolated H are found in interstitial positions (see Fig. 1): as positively charged H (H⁺) in the bond-center site (BC) if the material is *p* doped and as negatively charged H (H⁻) in a tetrahedral site (*T*) for *n*-doped Si. Isolated H in Si is a "negative-*U*" impurity: as the Fermi level is raised, H⁺ changes its charge state to H⁻, whereas H⁰ is never the lowest-energy state.^{2,3} However, such a result, which suffers a large computational uncertainty, has been criticized by other authors.⁴

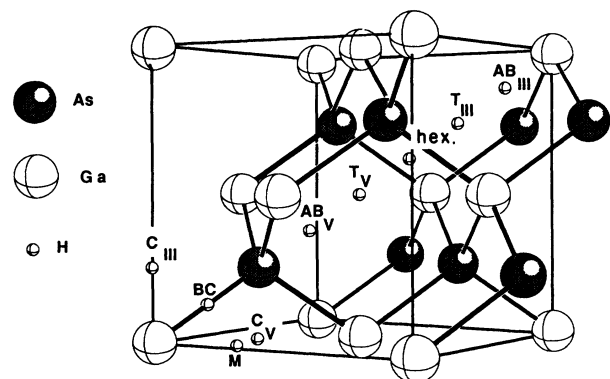


FIG. 1. Relevant interstitial sites for H in GaAs. BC .. the bond center, *T* the tetrahedral site (the subscripts III or V indicate the first-nearest-neighbor atom), AB the antibonding site, hex. the hexagonal site, *C* the C sites defined as the center of the rhombus formed between three adjacent atoms and the nearest *T* site, and *M* the site which lies on a line perpendicular to the Ga-As bond between the BC site and the neighboring hexagonal site.

The most stable form of H is the H_2 molecule, centered at the T site. While the H_2 molecule is essentially immobile, the so-called H_2^* complex, formed by one H in the BC site and one H in an antibonding (AB) or T position, has been proposed to play a role in H diffusion.³

Previous theoretical work on H in III-V materials has yielded some partial results, mainly based on a cluster approach.^{5–10} We report here the results of our detailed study of the properties of atomic and molecular H in undoped GaAs, with particular emphasis on the relative stability of the different forms of H. Some of our results about atomic H have already been published in Refs. 11 and 12.

This paper is organized as follows. In Sec. II we give a short description of our theoretical approach. In Sec. III we present our results for the relative stability of the H_2 molecule, the H_2^* defect, and the various charge states of isolated H. In Sec. IV we compare the indications from our results to available experimental data. Section V contains our conclusions.

II. THEORETICAL FRAMEWORK

A. Method

We have performed first-principles total-energy calculations, using supercells in the LDA with norm-conserving pseudopotentials in a plane-wave basis set. The H atoms are initially placed in some selected sites (see Fig. 1), and the forces acting on atoms calculated. Then, we let all atoms in the supercell relax to their equilibrium positions, by successive iterations, until the forces are smaller than a predefined quantity. Convergence tests show that reliable results can be obtained using 32-atom supercells, plane waves up to a kinetic energy of 12 Ry, and special points for the sum over the Brillouin zone which are equivalent to the two special points in the zinc-blende unit cell. This yields total energy differences which are converged to within 0.1 eV (0.2 eV in some difficult cases). However, we have found that 16-atom supercells can already yield reasonably accurate results. More technical details and a discussion of the convergence issue can be found in Ref. 11.

We have studied the stable sites and the relative stability of the H_2 molecule, the H_2^* defect (formed by one H in a bond-center site and one H in an adjacent tetrahedral position), and of three different charge states of atomic H, neutral (H^0), positive (H^+), and negative (H^-). As H^+ and H^- are described by charged supercells, which normally result in an infinite energy, we have added a neutralizing background, as in Ref. 2. In the practical implementation, the charge density and related quantities are computed with the desired number of electrons, while the electrostatic contributions (the so-called γ_{Ewald} and αZ terms) are computed as for the neutral system. In this way, the interaction between the extra charge and the neutralizing background vanishes as the supercell size grows.²

In all calculations, spin polarization—which is expected to be relevant only for neutral H—is neglected.

An *a posteriori* justification for this approximation can be found in Ref. 13, where spin-polarized calculations for H^0 show that the overall picture obtained in Ref. 11 by spin-averaged calculations is valid, and that spin polarization has only a minor effect in the energy-level structure.

B. Calculation of the formation energy

The formation energy of neutral species (H^0 , H_2 molecule, H_2^* defect) is simply obtained from total-energy differences. As total energies calculated in solids are not well converged, we compare total energies which are calculated exactly within the same approximations (i.e., with supercells of the same size, the same or equivalent k points, and the same cutoff for plane waves). In this way, we get energy differences which are much better converged than absolute energies. However, the neglect of spin polarization affects negatively the accuracy of the calculated energy differences between spin-polarized and spin-unpolarized configurations.

In a real semiconductor, a defect can exchange charges with a sea of electrons (coming from dopants or other defects) at the Fermi energy, μ . In particular, H^0 can lose or gain one electron and become a charged H^+ or H^- species. The formation energy of these charged species depends on the position of the Fermi level μ inside the gap. This, in turn, depends on the doping. Thus, we should calculate the occupancy level, i.e., those values of μ for which the stable charge state of H changes its electronic occupation number by one. This is not straightforward in a supercell calculation. We follow here the approach of Baraff, Kane, and Schlüter.¹⁴

Let us consider H^0 in its equilibrium lattice configuration R . H^0 induces a state in the band gap, containing $n = 1$ electron. We define the energy ε_+ (ε_-) as the additional energy necessary to remove (add) an electron to such a state, at fixed lattice:

$$\varepsilon_+ = E_{\text{tot}}(n = 0, R, \mu) - E_{\text{tot}}(n = 1, R, \mu), \quad (1)$$

$$\varepsilon_- = E_{\text{tot}}(n = 2, R, \mu) - E_{\text{tot}}(n = 1, R, \mu), \quad (2)$$

where $E_{\text{tot}}(n, R, \mu)$ is the total energy of the system for n electrons in the H-induced defect level in the gap and for a given Fermi level μ . Two other energy terms determine the occupancy levels. The first is the energy difference ΔE_R between the given charge state of H in the configuration R and in its stable site. The second term is the energy gained or lost while transferring electrons to and from the Fermi level on the defect level. We denote the total energy for the state H^0 as $E_0 = E_{\text{tot}}(n = 1, R, \mu)$ and put the zero of the Fermi energy μ at the top of the valence band. Then the formation energy E_F for the states of interest, H^+ , H^0 and H^- , are, respectively,

$$E_F = \begin{cases} E_0 + \Delta E_R^+ + \varepsilon_+ + \mu, & n = 0 & \leftarrow H^+ \\ E_0, & n = 1 & \leftarrow H^0 \\ E_0 + \Delta E_R^- + \varepsilon_- - \mu, & n = 2 & \leftarrow H^- \end{cases} \quad (3)$$

To compute ε_+ and ε_- we use Slater's transition-state

method.¹⁴ The occupation number n is treated as a continuous variable, and $E_{\text{tot}}(n)$ is regarded as an analytic function of n :

$$\varepsilon_+ = \int_1^0 \frac{\partial E_{\text{tot}}(n)}{\partial n} dn, \quad \varepsilon_- = \int_1^2 \frac{\partial E_{\text{tot}}(n)}{\partial n} dn. \quad (4)$$

The integral is approximated with the mean value:

$$\varepsilon_+ \approx \left[\frac{\partial E_{\text{tot}}(n, R, \mu)}{\partial n} \right]_{n=1/2}, \quad (5)$$

$$\varepsilon_- \approx \left[\frac{\partial E_{\text{tot}}(n, R, \mu)}{\partial n} \right]_{n=3/2}.$$

A general property of any local-density functional is that its derivative with respect to a particular occupation number is equal to the eigenvalue for that particular state.¹⁵ Thus ε_+ and ε_- are equal to the eigenvalues for the defect state in the gap, calculated with an occupation of $\frac{1}{2}$ and $\frac{3}{2}$, respectively.

III. RESULTS

Our results for the formation energy E_F are summarized in Fig. 2, where we compare the formation energies of the different defects studied in their stable lattice configuration. We have also included the results (dotted lines in the figure) obtained in Ref. 17 on the H-Si complexes in GaAs. We have taken the total energy of a GaAs supercell and an isolated H atom in vacuum as the zero of the formation energy scale.

In Fig. 2 three main results are evident: (i) the stable state of H in pure GaAs is the H_2 molecule, (ii) isolated H behaves as a negative- U defect, and (iii) in Si-doped GaAs (n or p type) the formation of H-Si complexes is in any case the most stable form for H.

A. Molecular hydrogen

We have studied several sites for the H_2 molecule along the $\langle 111 \rangle$ axis using a 16-atom supercell. In the following, we label the configurations with the initial position—before relaxation—of the center of mass of the H_2 molecule. Our results are summarized in Table I.

TABLE I. Molecular H in GaAs (16-atom supercell results). The zero of the energy is the energy of the stable site. The H-H distance ($d_{\text{H-H}}$) in the molecule before relaxation was 0.795 Å. The distances $d_{\text{H}_2\text{-Ga}}$ and $d_{\text{H}_2\text{-As}}$ are referred to the center of mass of the molecule in the $\langle 111 \rangle$ direction. The numbers within parentheses refer to the distances before lattice relaxation.

H_2 site	Energy (eV)	$d_{\text{H-H}}$ (Å)	$d_{\text{H}_2\text{-Ga}}$ (Å)	$d_{\text{H}_2\text{-As}}$ (Å)
BC off axis $\langle 100 \rangle$ oriented	2.29	0.93	1.68 (1.21)	1.94 (1.21)
hexagonal $\langle 100 \rangle$	0.95	0.79	3.64	3.66
hexagonal $\langle 111 \rangle$	0.96	0.78	3.63 (3.64)	3.67 (3.64)
T_V $\langle 100 \rangle$	0.13	0.82		2.43
T_V $\langle 111 \rangle$	0.12	0.81		2.47 (2.43)
T_{III} $\langle 100 \rangle$	0.00	0.82	2.43	
T_{III} $\langle 111 \rangle$	< 0.01	0.81	2.55 (2.43)	

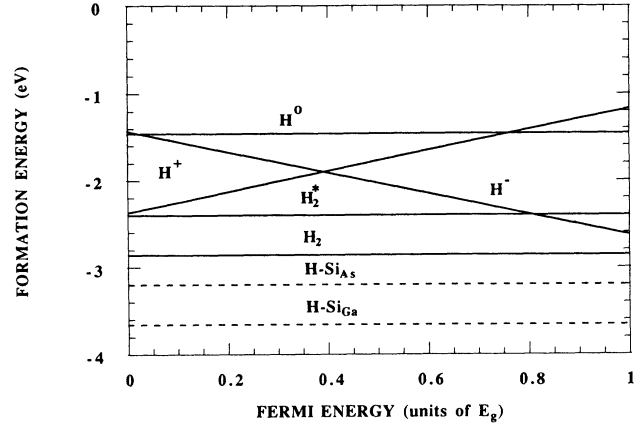


FIG. 2. Formation energy of the different charge states of H and of molecular H_2 in GaAs as a function of the Fermi energy. The Fermi energy is given in units of $1/E_g$, where E_g is the computed GaAs energy gap (1.2 eV). H_2^* is the complex formed by a H atom in a BC site and a H atom in a T_V site. H^+ is the positively charged, H^- the negatively charged, and H^0 the neutral state of H. The dotted lines refer to the H-Si complexes with a Si atom substituting for a Ga atom (Si_{Ga} donor) or an As atom (Si_{As} acceptor). The zero of the formation energy is the energy of a GaAs supercell and an isolated H in vacuum. The units are eV/H atom. The zero of the Fermi energy is the top of the valence band. The results are for a 32-atom supercell.

The stable site is the H_2 molecule in the T_{III} site, with the $\langle 111 \rangle$ and $\langle 100 \rangle$ orientations for the molecule almost degenerated in energy. The bond length of the molecule oriented along the $\langle 111 \rangle$ axis is 0.81 Å, slightly larger than the LDA value for an isolated molecule calculated within the same approximations: 0.795 Å (experimental value 0.75 Å). The center of mass of the molecule moves by 0.06 Å in the $\langle 111 \rangle$ direction from the T_{III} site towards the nearest Ga atom which in turn moves by 0.07 Å away from the H_2 molecule. The relaxation deforms the zincblende cube, which becomes a rhombus elongated in the $\langle 111 \rangle$ direction. The lattice relaxation lowers the configuration energy by 0.2 eV. For the $\langle 100 \rangle$ orientation of the molecule, the center of mass of the molecule does not move, and the bond length enlarges to 0.82 Å.

Other sites for the H_2 molecule have been studied. The T_V site is only 0.13 eV higher in energy than the T_{III} . The length of the molecular bond is 0.81–0.82 Å depending on the orientation, as for H_2 in the T_{III} site. In the $\langle 111 \rangle$ orientation, the center of mass of the molecule approaches only 0.01 Å to the nearest-neighbor As atom. This indicates a lower interaction with the neighboring atoms than in the T_V site. No center-of-mass motion occurs when H_2 is oriented along the $\langle 100 \rangle$ axis. To move from the T_{III} to the T_V site, H_2 passes through the Hex site finding a barrier higher than 1 eV.

H_2 oriented long the $\langle 111 \rangle$ axis in the hexagonal site has a large energy and the bond length is 0.78 Å. The distance between the H in the molecule and the nearest Ga or As atoms in the $\langle 111 \rangle$ direction is 3.63 and 3.67 Å, respectively. The center of mass moves by 0.02 Å towards the Ga atom. This site is a saddle point of the energy surface.

When the H_2 molecule is placed in the BC oriented along the $\langle 100 \rangle$ axis, its energy is about 2 eV higher than in the T_{III} site. The bond length of the molecule is 0.93 Å, while the host Ga-As bond is stretched to 3.62 Å. The distances between the center of mass of the molecule and the Ga or As atoms are 1.68 and 1.94 Å, respectively.

The H_2 molecule in its stable site inside GaAs has an energy 0.5 eV higher than in free space. Thus we expect that H_2 does not penetrate into the GaAs lattice. Atomic H^0 in its stable site inside the crystal is instead 1.45 eV lower in energy than in free space,¹¹ so H penetrates into the GaAs lattice in atomic form. Once atomic H has diffused in the lattice, however, it proves convenient to form molecules: the formation energy of a H_2 molecule from two H^0 , in their respective equilibrium sites, is -2.8 eV. Such results have been obtained using more accurate 32-atom supercells.

B. The H_2^* defect

Two H atoms in nearby lattice positions generate the so-called H_2^* defect.¹⁶ Several configurations for H_2^* have been studied using a 16-atom supercell (see Table II). This defect is preferentially formed by a H atom in the T_{III} site and a H atom sitting in the BC site. In GaAs this defect has an energy 1 eV higher than the H_2 molecule in the T_{III} site. The Ga-As bond passes from 2.42 to 3.54 Å, mainly because the Ga atom moves and binds to the H in the T_{III} site (the Ga-H distance is 1.63 Å). The distance of the H atom in the BC site with the Ga atom is 2.02 Å whereas that with the As atom is 1.53 Å. The electronic charge density (Fig. 3) shows that the Ga-

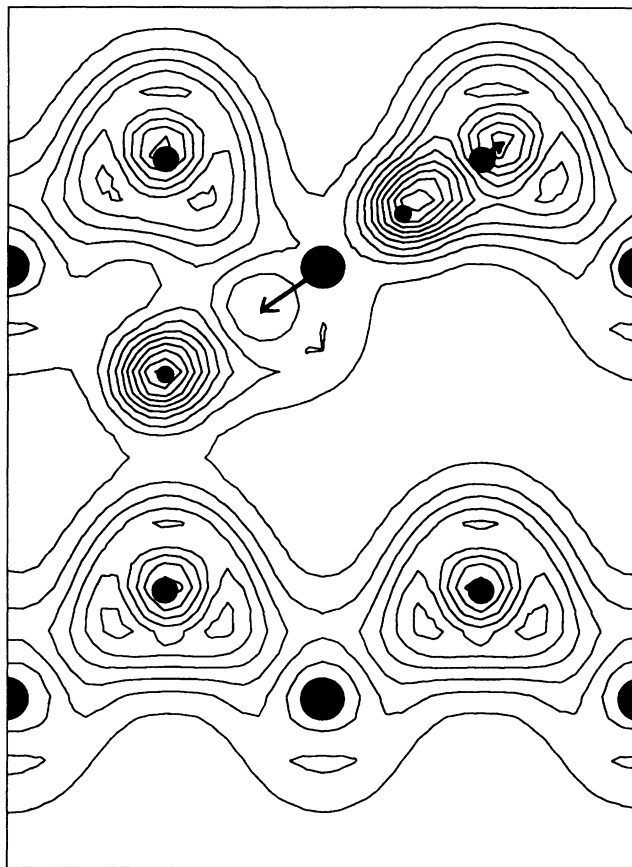


FIG. 3. Contour plot in the (110) plane of the valence-charge density for the H_2^* defect formed by a H^0 atom (indicated in the figure by a small solid circle) in the BC and a H^0 atom in the T_{III} site, after lattice relaxation. The new positions of H^0 and of the nearest atoms after the relaxation are indicated by the arrow tip. The unrelaxed atomic positions of the Ga and As atoms are indicated by solid circles (the bigger ones are for Ga).

As bond is almost broken and the H atom in the BC site behaves like H^+ , which binds to the more electronegative As atom (see later). The surplus electron is taken by the Ga atom which binds to the H atom in the T_{III} site. The final configuration of the Ga-H complex is very similar to that of the H-donor complex in GaAs.¹⁷

The configuration with a H atom in the BC site and a H atom in the T_V site is 0.2 eV higher in energy. The H_2^* defect formed by two H atoms in two parallel BC sites has a much higher energy, about 3.6 eV above the H_2 molecule.

C. Isolated H

The energetic for H in the different charge state is summarized in Table III (see also Refs. 11 and 12). Calculations for 32-atom supercells have been made only for H^0 and for some selected sites of H^- and H^+ . The comparison of results from 16- and 32-atom supercells gives a hint on the importance of the cell size. While the general fea-

TABLE II. H_2^* defect in GaAs (16-atom supercell results). The zero of the energy is referred to the stable site of the molecule (Table I)

H_2^* site	Energy (eV)
T_V - BC	1.14
T_{III} - BC	0.93
BC-BC (parallel)	3.64

TABLE III. Total-energy differences in eV for atomic H in unrelaxed (U) and relaxed (R) GaAs. Three different charge states of H are reported: H^- is the negative charged state, H^+ is the positive charge state, and H^0 is the neutral charge state. The results have been obtained using a 16-atom supercell except for the first two rows where a 32-atom supercell has been used. The zero of the energy is at the global minimum for each H charge state. The different columns correspond to the results for H in different high-symmetry interstitial sites (see Fig. 1 for the meaning of the notations).

	BC	C_{III}	C_V	AB_{III}	AB_V	M	H	T_{III}	T_V
H^0 (U)	5.22	1.24	1.32	2.34	2.34	1.08	0.26	0.33	0.26
H^0 (R)	0.19	0.11	0.21	0.23	0.00	0.11	0.25	0.29	0.22
H^0 (U)	5.10	0.84	1.28	2.20	2.21	0.88	0.13	0.40	0.33
H^0 (R)	0.46	0.00	0.28	0.19	0.03	0.04	0.10	0.38	0.30
H^+ (U)	4.69	1.29	0.96	2.92	2.42	0.94	0.98	1.86	1.56
H^+ (R)	0.09	0.34	0.17	1.25	0.34	0.00	0.91	1.85	1.43
H^- (U)	6.59	2.39	2.63	3.16	3.55	2.30	0.71	0.25	0.46
H^- (R)	0.96	0.42	0.00	0.07	0.42	0.66	0.07	0.10	0.42

tures of the energy surface can be obtained already from 16-atom supercells, such a cell is too small to get accurate results when a large lattice relaxation takes place, hence to calculate energy differences or energy levels (Fig. 2) we have used a 32-atom supercell.

When the lattice is not allowed to relax, H finds its low-energy state in the low-valence-charge (LVC) density region (the T and hexagonal sites), and it is disfavored in the high-valence-charge (HVC) density region (all other sites).

When the lattice is allowed to relax, the picture changes dramatically. In general, H induces a weak relaxation when it is placed in the LVC region, a sizable one in the HVC region, and a very strong one when it is placed in the BC site.¹¹ After relaxation, H^+ is most likely to be located at the BC site in the HVC region, H^0 an AB site in the HVC region, and H^- at a T site in the LVC region. Energy differences among LVC and HVC sites are quite big for H^+ , smaller for H^- , and very small for H^0 , which has a very flat energy surface.

The formation energies of the different charge states of isolated H, obtained as explained in Sec. II B, are plotted in Fig. 2 as functions of the Fermi energy μ . The uncertainty in LDA energy levels and the finite supercell size make the error bar very large on the data shown. We estimate an error of at least 0.2 eV, because the calculated energy gap for GaAs is 1.2 eV, versus 1.52 eV measured at 2 K, and also because the impurity-induced level in the gap has a dispersion of about 0.1 eV.

Our results indicate that H in GaAs forms a negative- U system, as in Si.^{2,3} Such terminology comes from the correlation energy U in the Anderson model, which is usually a positive quantity, as a consequence of Coulombian repulsion between electrons on the same site. In a negative- U system, the level occupancy changes by two units (instead of one as in a positive- U system) as the Fermi energy is raised above the level. In our case, the sequence of equilibrium states is H^+ followed by H^- as the Fermi energy is raised, while H^0 is never the stable state of lowest energy. Lattice relaxation is essential in determining the negative- U character of a defect.

If the Fermi level is situated at the bottom of the conduction band (n -doped GaAs), the stable charge state is H^- . H^- is most likely to be found in the LVC region and at the sites which have Ga (the less electronegative atom) as nearest neighbor. When H^- is initially placed in the C_V , in the AB_{III} , and in hexagonal sites, it tends to move towards the T_{III} site. In these sites, an acceptor level is formed in the band gap. The other sites have higher energies, with the BC the less-probable site. In the BC, H^- is 1.54 Å from the Ga and 2.05 Å from the As atom. H^- diffuses in the LVC region (which includes in this case the C_V , the AB_{III} , the hexagonal, and the T_{III} sites). Such a picture is very similar to the one found for Si, where H^- prefers the T sites, while the hexagonal site is some 0.2 eV higher in energy.^{2,3}

If μ is at the top of the valence band ($\mu=0$), the stable charge state is H^+ . H^+ is most likely to be located in the HVC region, and binds preferentially to the more electronegative As atom: in the BC site H^+ is 1.80 Å from the Ga and 1.52 Å from the As atom [a value close to the bond length in arsine: 1.519 Å (Ref. 18)]. There are three almost degenerated low-energy configurations, the BC, the M , and the C_V sites. Larger supercells yield lower BC site energies with respect to other sites as the lattice relaxation is better accounted for (see, e.g., the results for H^0 in Table III). A diffusive path for H^+ is found between the BC through the M and the C_V sites in the HVC region [as for H^+ in Si (Ref. 2)]. In these sites H^+ induces the formation of a deep donor level. The energy differences between the LVC and HVC regions are higher in GaAs than in Si (where they are about 0.5 eV),² because of the long-range Coulombian attraction between the more electronegative As atoms and H^+ .

We can give a simple picture of the findings given in Fig. 2 for atomic H.¹⁹ When H enters into n -doped GaAs, it traps one extra electron to fill the 1s shell and becomes negatively charged. H^- is quite inert as it reaches the electronic configuration of He. In this case the LVC sites, where the interaction with the lattice is weak, are preferred. For p -doped GaAs, no free electrons are available, and H interacts strongly with the lattice due to the

unfilled $1s$ shell. The HVC region is now preferred. Hydrogen in the BC site induces the formation of a three-center bond.²⁰ For p -doped GaAs (μ at the top of the valence band), the energy gain in the formation of the three-center bond is larger than for H^0 because the empty donor level is pushed deep in the band gap and the energy cost to relax the bond is lower, because less charge is piled up in the bond than in undoped GaAs. As a consequence of the balance between these two quantities, H^+ in the BC is the favored charge state.

Although direct experimental confirmations are needed to support the negative- U character of H^0 , our theoretical findings could explain the lack of experimental evidence for the presence of isolated neutral H in GaAs. Isolated H^0 would be paramagnetic, but to date there is only one observation of isolated H^0 in Si by electron paramagnetic resonance (EPR).²¹ No absorption in the far-infrared region from isolated H^0 has been reported. This suggests two possibilities: either isolated H^0 has a very high diffusivity and a very strong tendency to form complexes, or it is an unstable charge state.²²

An interesting property of a negative- U defect is the possibility of disproportionation, i.e., transfer of charge from one isolated H^0 atom to another. In particular, in GaAs we could have



where H^0 is in an AB site, H^+ is in a BC site, and H^- is in a T site. Once formed, these charged pairs could either interact with defect or attract each other forming H_2 or H_2^* . In the latter case the two H atoms are self-compensating.²³

D. H in other semiconductors

Supercell calculations in the framework of first-principles LDA-pseudopotential techniques have been ex-

tensively used to study the properties of H in Si.^{2,3} The main features of the behavior of H in Si are similar to those found for H in GaAs (compare, e.g., Fig. 2 to Fig. 3 of Ref. 3). In both materials, H is a negative- U impurity (but other authors⁴ disagree with such a conclusion for Si); H^0 has an extremely flat energy surface; the stable state is the molecule H_2 . In Si, the T site is the stable site for the molecule H_2 which is oriented along the (100) direction with a bond length of 0.86 \AA and a dissociation energy of about 2 eV .^{3,2} In the hexagonal site, the energy is 1.1 eV higher than in the T site. The behavior of H_2 is very similar for GaAs and Si, as one could expect from the fact that the interaction of H_2 with the lattice is very small in semiconductors.

However, some differences can be found between the behavior of H in GaAs and that of H in Si. We consider here the results of Ref. 2 because of the similar approximations done. In Si, H tends to be symmetrically located with respect to neighboring Si atoms, whereas in GaAs, H^+ tends to interact more strongly with As atoms, H^- and, to a lesser extent, H^0 , with Ga atoms. H^0 and H^+ have similar features in Si, much less in GaAs. In GaAs, H^0 has the stable state in AB_V , whereas in Si, the BC site is the lowest-energy site for H^0 . This is a consequence of the higher bond strength of GaAs with respect to Si: the energy gained in the formation of a three-center bond in the BC is not sufficient to make this site more stable than the AB_V site, where H^0 binds to the As with less stretching of the bond than in the BC site.

In Table IV we compare the properties of neutral H in the BC site of several III-V semiconductors, plus Si as the prototype of elemental semiconductors. A trend can be deduced from Table IV. As the bond strength or the ionicity of the compound increases, the energy of H^0 in the BC site increases with respect to the energy of the stable H^0 site. In particular, the BC site is the stable site for H^0 in Si, whereas in AlAs it has a higher energy (0.55 eV higher from the LDA, 0.36 eV from Hartree-Fock

TABLE IV. Comparison between the lattice relaxation induced by H^0 in the BC site of different semiconductors. The first three rows report results from a LDA-supercell calculation (32-atom supercell for GaAs and Si, 16-atom supercell for AlAs). The remaining rows report Hartree-Fock cluster results. E_g is the experimental energy gap at $T = 0 \text{ K}$, f is the experimental Pauling ionicity character computed as $f = 100[1 - \exp(-\Delta X/4)]$, where ΔX is the difference between the electronegativity of the two component atoms, d_{III-H} and d_{V-H} are the computed distances of H with its first neighboring atom (for Si atoms are equal), ΔE_r is the computed energy gain in the lattice relaxation, and ΔE is the computed energy difference between the most stable site for H in the semiconductor and H in the BC site.

	E_g (eV)	f	Bond relaxation %	d_{III-H} (\AA)	d_{V-H} (\AA)	ΔE_r (eV)	ΔE (eV)	Ref.
Si	1.17	0	38	1.63	1.63	> 4	0.0	2
GaAs	1.51	9.5	40	1.68	1.72	5.0	0.19	this work
AlAs	2.23	13.9	50	2.09	1.72	4.6	0.55	24
Si	1.17	0	35	1.59	1.59		0.00	9
InP	1.42	9.5	34.5			3.75		7
GaAs	1.51	9.5	34.5	1.68	1.61	4.02		6, 7
GaP	2.35	11.8	37			4.27		7
AlP	3.0	13.9	45	1.43	1.75		0.36	9

calculations) with respect to the stable site. Moreover as the band-gap energy increases, the bond relaxation increases. For LDA calculations it passes from 38% for Si to about 50% for AlAs. For Hartree-Fock calculations it passes from about 34% for GaAs to about 45% for AlP.

IV. COMPARISON WITH EXPERIMENTAL DATA

A. General passivation features

It has been experimentally found that a region near the surface is characterized by a very high H solubility.¹ The profiles of deuterated samples, measured by SIMS, show an accumulation of H in this near surface region with H concentration in excess of 10^{19} cm^{-3} . Thermal treatments do not modify the H profile in this highly doped region.²⁵ Transmission electron microscopy studies have revealed the formation of H platelets. In Si several models associated aggregates of H_2^* with these platelets.¹⁶ Our calculations show that the stable form of H in GaAs is an immobile form which comes from the interaction of atomic H, once it enters into the lattice. This result is in agreement with experimental data.

For doped GaAs, the diffusion depths and H concentrations are larger in *p*-type GaAs than in *n*-type GaAs.²⁶ Semi-insulating material shows a H concentration profile similar to that of lightly *n*-doped GaAs. The binding of H with impurities or defects is more effective for *n*-type GaAs than *p*-type GaAs.²² Acceptor passivation is less stable than that of donors. These facts are in agreement with our findings. The formation of a H-acceptor complex requires a stronger lattice relaxation (H^+ has the stable energy site in the BC) than the formation of a H-donor complex (H^- has the stable energy site in the LVC region).¹⁷ Moreover, H^- in *n*-doped GaAs has a lower formation energy than H^+ in *p*-doped GaAs (see Fig. 2). In undoped GaAs (μ in the middle of the band gap) the stable charge state is H^- as in *n*-doped GaAs, thus H behaves essentially in the same way in undoped or *n*-doped GaAs.

B. Charge-state stability

An attempt to determine the charge state of H during the diffusion has been performed by SIMS studies on selectively doped samples.²⁶ It has been found that a cap layer of highly doped *n*-type GaAs inhibits the diffusion of H in GaAs. A retardation effect is observed both in *p*-doped and *n*-doped GaAs. On the other hand, no similar effect is observed when the cap layer is *p*-type. The authors explained their observations with the existence of a donor level induced by H in the upper half of the band gap. In this model H behaves as positively charged H in *p*-doped GaAs and as neutral charged H in undoped or *n*-doped GaAs.

The main experimental data about the charge-state stability in *n*- or *p*-doped GaAs have been reported using the reverse-bias-annealing (RBA) technique. This

method is based on the study of the profile of reactivated impurities after annealing H-passivated samples. In order to distinguish between the different charge states an electric field is applied. The field is provided by the polarization of a Schottky contact. Both Si- or Se-doped *n*-type samples and Zn-doped *p*-type samples have been studied.^{25,27-29}

In Ref. 27, RBA experiments were performed on Zn-doped GaAs. The experimental results show that a mobile, monatomic species exists. Considering the electric field due to the polarization of the Schottky diode, the authors concluded that they have observed the drift of a positively charged species. More interestingly, RBA experiments show that the high concentration feature near the surface is immobile even though atomic deuterium moves deep in the sample. This fact indicates that the species forming this high concentration region is neutral and consequently supports the conclusion that H aggregates, like molecules, are formed in this region.

Several recent papers reported about RBA experiments on *n*-doped GaAs.^{25,28,29} Experimental evidences have been presented about the existence of H in a negatively charged state in *n*-doped GaAs. All the RBA study performed on Si or Se-doped GaAs observed that the measured carrier-concentration profiles may be explained by the field-assisted drift of a negatively charged H species.

In summary, RBA experiments support the findings about the stable charge state given in Fig. 2 when the Fermi level is close to the valence-band edge or the conduction-band edge, but do not provide informations about the negative-*U* property of H.

C. Energy levels induced by H in the band gap

Only a few studies concern the occupancy levels for H in GaAs.³⁰⁻³³ In Ref. 30 by the Fermi dependence of the localized vibration mode (LVM) of the C-H complex it is found that an occupancy level exists at $\mu \simeq E_v + 0.5 \text{ eV}$, where E_v is the top of the valence band. This level corresponds to a transition level between a positive charge state of H and another charge state. Unfortunately, the experimental data do not settle if the transition is a one-electron or a two-electron one. Initially, by comparison with a far-infrared absorption spectrum of a highly *n*-doped sample, Clerjaud *et al.* concluded that the $E_v + 0.5 \text{ eV}$ level should be associated with a two-electron transition and located midway between the H-acceptor and the H-donor level.³⁰ Recently, by analyzing SIMS profiles, the same authors proposed that the measured level is the transition level between the positive and the neutral charge state of H, i.e., the donor level induced by H.³¹

This last conclusion is supported by a model calculations of the SIMS profiles of doped GaAs.^{32,33} In Ref. 32 the SIMS profile of Zn-doped GaAs have been fitted assuming that H diffuses both in the positive and in the neutral charge state. The relative densities are in thermal equilibrium with the donor level induced by H^+ at $E_v + (0.4 \pm 0.05) \text{ eV}$, in very good agreement with the re-

sults of Clerjoud *et al.*³⁰ For undoped and *n*-doped GaAs, the SIMS profiles do not show a plateau as in *p*-doped GaAs. This should indicate the absence of the long-range Coulomb interaction between H and the ionized donors. The SIMS data are well described by a model where the diffusing species is neutral H and which yields an error function profile.³³ In $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys the characteristic plateau in the deuterium concentration forms at $x > 0.06$. From these data Chevallier and Pajot³³ concluded that for $x > 0.06$ the diffusing species is H^- and that the related acceptor level induced by H in GaAs is resonant with the conduction band at about 0.08 eV above the conduction-band minimum. Hence this SIMS analysis favored a positive-*U* character for H.

However a note of caution is necessary about the analysis of SIMS data. In fact (i) the deuterium profile depends strongly on the initial condition of the sample surface and on the parameters used during the plasma exposure;²⁶ (ii) this analysis of the SIMS data is in contradiction with the RBA measurements; (iii) CV measurements in *n*-doped GaAs indicate an active role of a charged impurity;²⁵ (iv) the absence of a plateau in the SIMS profile is not necessarily connected with the diffusion of a neutral species. In fact, multitrapping of charged H to the same impurity site leads to diffusion profiles which have exponential shapes.³⁶ During a RBA experiment, the species formed by the dissociation of the H-dopant complexes are driven away by the presence of the electric field in the depletion layer of the diode. On the contrary, in usual diffusion experiments the situation is complicated by the presence of several species (at least the formation of a H_2^* defect or a H_2 molecule).

D. Comparison with the results of muon measurements

Muonium is a light pseudoisotope of H.³⁴ Even though muonium presents a larger zero point motion than H and a short lifetime ($\simeq 2 \mu\text{sec}$), a comparison with our results is possible. For our discussion, two paramagnetic species of muonium are interesting, Mu and Mu^* . Mu^* , also called anomalous muonium, has the characteristic of an anisotropic center. In the literature it has been interpreted as a muonium in a BC site. Mu, or normal muonium, has an isotropic character and is usually associated with a muonium in a tetrahedral site. The trends given in Table IV have an experimental counterpart in the relative stability of the different forms of muonium (see Table VIII in Ref. 34). As the bond strength increases the relative occurrence of Mu^* decreases while that of normal Mu increases.

In GaAs, a large lattice relaxation associated with Mu^*

is experimentally found.³⁵ Our calculations for H^0 in the BC site give a bond relaxation comparable with the experimental results for anomalous muonium. Mu^* , at the bond center, induces a relaxation of $(32 \pm 7)\%$ in the bond length (we find a relaxation of 40%), and the As and Ga atoms are displaced (0.65 ± 0.17) and (0.14 ± 0.06) Å away from the bond (our results are 0.66 Å for As and 0.31 Å for Ga). Concerning the normal muonium, it has been found that it is extremely mobile and stays in an isotropic cage with Ga atoms as first neighbors. Our findings of a stable site for H^0 in the *T* sites when no lattice relaxation is allowed could explain the data for normal Mu. Finally, our results that the stable site for H^0 in GaAs is not the BC site can also be supported by the observation that a thermal conversion from Mu to Mu^* has not been observed for muonium in GaAs. On the contrary it has been measured in Si, which indicates that Mu^* is more stable than Mu.³⁴

V. CONCLUSION

Using first-principles calculations we have investigated the behavior of atomic and molecular H in GaAs. We have found that lattice relaxation plays a very important role in stabilizing the different forms of H. The stable form of H in pure GaAs is an immobile H_2 molecule with the two H atoms in a *T* site and with a very small interaction with the host Ga or As atoms. The balance between bonding and stretching is relevant in favoring the high-valence-charge or the low-valence-charge sites as the stable position for atomic H. We have found that in *n*-doped GaAs atomic H behaves as an acceptor and sits in a *T* site with a small interaction with the lattice. In *p*-doped GaAs, a bond rearrangement stabilizes positively charged H in the BC site where it acts as a donor. A mid-gap occupancy level induced by H has been found which corresponds to a two-electron transition from H^+ to H^- . The energy value of this level agrees surprisingly very well with the energy of a transition level measured experimentally. However, this agreement might be fortuitous as the uncertainty in the theoretical results are quite large. A still open question is whether the theoretical predictions of the negative-*U* nature of the H impurity, in both GaAs and Si, will be confirmed by experiments.

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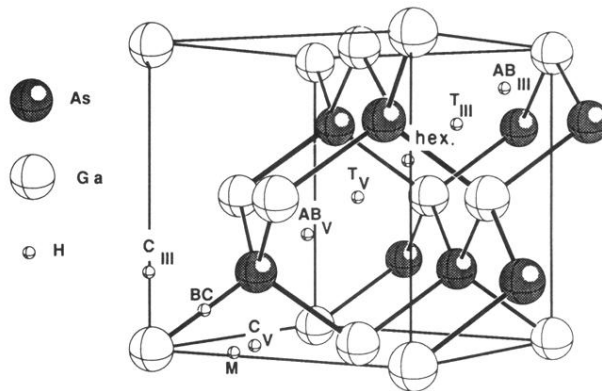


FIG. 1. Relevant interstitial sites for H in GaAs. BC is the bond center, T the tetrahedral site (the subscripts III or V indicate the first-nearest-neighbor atom), AB the antibonding site, hex. the hexagonal site, C the C sites defined as the center of the rhombus formed between three adjacent atoms and the nearest T site, and M the site which lies on a line perpendicular to the Ga-As bond between the BC site and the neighboring hexagonal site.