Theory of hydrogen-decorated gallium vacancies in GaAs and of their radiative complexes

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Complexes formed by neutral or charged Ga vacancies and one or more H atoms have been investigated by using a pseudopotential-local-density-functional approach. Stable and metastable configurations have been found with some hydrogen atoms saturating As dangling bonds around the Ga vacancy. In this case, the electronic energy levels of the vacancy, although slightly lowered toward the valence band, remain in the energy gap. When one H atom is located at a bond center position next to a H-decorated vacancy, a donor level appears in the energy gap. The donor-acceptor pairs formed by this H atom and the Ga vacancy can account for the low-energy luminescence bands reported in hydrogenated p-type GaAs.

I. INTRODUCTION

The introduction of atomic hydrogen into the lattice of covalent semiconductors leads to the neutralization of the electrical activity of both deep and shallow defects, i.e., to the removal of all their electronic levels from the energy gap.[1] In particular, a passivation of deep levels has been achieved in crystalline silicon, c-Si, in the case of complexes including sulfur and oxygen atoms.[1] The same results hold in intrinsic GaAs, where hydrogen passivates deep levels like those of the DX (Ref. 2) and of the $EL2$ (Ref. 3) centers.

A typical "intrinsic" defect is obtained when an atom is removed from the lattice of a semiconductor. The resulting vacancy gives rise to energy levels deep into the gap, as shown for the silicon vacancy (V_{Si}) in c-Si (Ref. 4) and for the gallium vacancy (V_{Ga}) in GaAs.[5] Under atomic hydrogen irradiation, vacancies may exhibit a quite different behavior from that of other deep defects, depending on the host material. In the case of V_{Si}, theoretical and experimental studies have shown that a partial saturation of the Si dangling bonds with H atoms starts to lower the corresponding vacancy states toward the valence band, until a full passivation is achieved when all the four Si dangling bonds in the vacancy are saturated.[6] In intrinsic GaAs, hydrogen saturates the As dangling bonds surrounding the Ga vacancies, as supported by infrared absorption measurements, which have related a localized vibrational mode at 2001 cm^{-1} to a As-H bond in a gallium vacancy.[7] However, *hydrogenation never fully removes the V_{Ga} energy levels from the energy gap*, as has been shown recently by the observation of a photoluminescence (PL) band in hydrogenated slightly p-type GaAs at an energy much lower than that of the optical gap.[8,9] This band has been explained in terms of a donor-acceptor (D-A) band, the acceptor state being provided by the V_{Ga}, the donor state by the hydrogen atom. For increasing excitation power, several bands have been observed at energies higher than that of the first band. They have been related to the differing charge states of the Ga vacancy, thus allowing an estimate of the energies of the corresponding electronic levels. It has to be mentioned here that Ga vacancies are optically inactive in intrinsic GaAs, while they have been observed in photoluminescence experiments in highly doped n-type GaAs. There the Ga vacancies form stable complexes with the donors and give rise to a D-A recombination band[10] at energies that depend on the donor type and are very close to that lately observed in hydrogenated slightly p-type GaAs.[8,9] In conclusion, contrary to what is reported in the V_{Si} case, hydrogen activates optical transitions from a H-related donor state to the vacancy levels, which are not removed from the energy gap.

On the theoretical side, the isolated V_{Ga} (without hydrogen) has been studied either taking into account or disregarding lattice relaxation effects. In the latter case, tight-binding approaches have found different electronic eigenvalues in the energy gap for different states of charge of the vacancy.[11,12] In the former case, *ab initio* methods show instead that the electronic eigenvalues of the vacancy are almost independent of the degree of charge of the vacancy.[13] To our knowledge, the case of complexes formed by hydrogen atoms and Ga vacancies in GaAs has never been studied.

The aim of the present work is to investigate the properties of gallium vacancies decorated by hydrogen saturators H_s of the As dangling bonds, and to evaluate their equilibrium geometries, stabilities, and electronic structures. Partial or total saturation of the As dangling bonds will be achieved, with no removal of the vacancy levels from the energy gap. Stable complexes formed by a H atom near the center of a Ga-As bond, H_{BC}, and

a nearby isolated or H-decorated V_{Ga} will be then investigated, showing that a deep donorlike state in the energy gap is induced by H_{BC}. *D-A* pair transitions result from the H-induced state and the acceptor levels of V_{Ga}. The estimated electronic eigenvalues of the H_{BC}-V_{Ga} complexes will be finally compared with those obtained in the case of isolated vacancies as well as with the values of the energy levels as determined from PL experiments.

II. METHODS

The equilibrium geometries of different complexes formed by gallium vacancies and hydrogen atoms have been investigated by performing *ab initio* total energy and force calculations in the local-density-functional (LDF) framework within a supercell approach.[14,15] The geometry of supercells containing one or more H atoms and one V_{Ga} has been fully relaxed by minimizing the Hellmann-Feynman forces on the atoms[16] through an estimate of the dynamical matrix.[17] The exchange-correlation functional of Ceperley-Alder[18] has been used together with norm-conserving pseudopotentials[19] and plane-wave basis sets; **k**-space integration has been performed with the use of the special-point technique.[20] Convergence tests have been done by using plane-wave cutoffs ranging from 12 to 16 Ry, supercells of 16, 32, and 64 atoms, and **k**-point meshes equivalent to a (4,4,4) or (8,8,8) Monkhorst-Pack mesh in the zinc-blende unit cell. Satisfactorily converged total-energy and atomic-force values have been achieved by using 32-atom supercells, the (4,4,4) **k**-point mesh, and the cutoff of 12 Ry. A rough estimate of the vacancy-energy-level position in the gap has been obtained by taking a weighted average of the electronic eigenvalues over several high symmetry points in the Brillouin zone. A dispersion of 0.2 eV of the electronic eigenvalues in the energy gap is typically observed in the 32-atom supercell, only slightly higher than that obtained in the 64-atom supercell. The 32-atom supercells have then been used to investigate the electronic structure of the vacancy. Furthermore, the 16 Ry cutoff on the kinetic energy has been used for the calculation of the electronic eigenvalues, lower cutoffs would lead to an indirect energy gap for "perfect" GaAs. A neutralizing background has been introduced when dealing with charged supercells. A Gaussian broadening scheme[21] has been used to deal with the Fermi surface whenever the unit cell contained an odd number of electrons. More details about the calculation procedures can be found elsewhere.[22]

III. RESULTS AND DISCUSSION

The electronic configuration of the V_{Ga} consists of a filled a_1 state, deep in the valence band, and of a threefold-degenerate half-filled t_2 state in the GaAs energy gap,[5] which accounts for the triple acceptor nature of the V_{Ga}, see Fig. 1. Hence, complexes involving H atoms and the neutral or the three negatively charged states of the isolated Ga vacancy, V_{Ga}^0, V_{Ga}^{-1}, V_{Ga}^{-2}, and

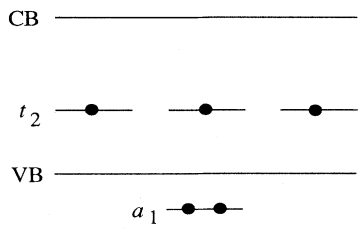

FIG. 1. Schematic illustration of the electronic levels of a neutral Ga vacancy.

V_{Ga}^{-3}, have been considered in the present work. In particular, a number of configurations where a H atom is located at a BC site, H_{BC}, next to an isolated vacancy or to a vacancy decorated by H saturators, has been investigated. Isolated vacancies will be briefly discussed in the first part of the present section, hydrogen-decorated vacancies in the second part, and complexes containing a neutral or ionized H_{BC} atom next to a vacancy in the third part. The most favorable configurations of complexes containing both H_s and H_{BC} atoms will be discussed in the fourth part of the section. Finally, a comparison with experimental results and other theoretical models will be made in the fifth and last part of this section.

A. Isolated gallium vacancies

The case of isolated charged vacancies has been investigated allowing for a relaxation of the lattice. In agreement with a previous theoretical study,[13] the stable configurations are characterized by a "breathing" relaxation, i.e., by a radial shift toward the vacancy of the four nearest-neighbor As atoms with no sizable pairing between them. The radial shift, already sizable for the neutral vacancy (0.16 Å), increases with the negative charge n on the vacancy (0.24 Å for n=3). Since the local tetrahedral symmetry of the "perfect" GaAs is substantially preserved, the electronic structure of the relaxed vacancy is still characterized by the presence of a threefold-degenerate t_2 state originating from the p atomic orbitals of the As atoms. The vacancy levels are located 0.690, 0.704, 0.721, and 0.734 eV above the top of the valence band in the case, respectively, of V_{Ga}^0, V_{Ga}^{-1}, V_{Ga}^{-2}, and V_{Ga}^{-3}. (The energy gap calculated for GaAs is 1.4 eV.[23]) These results well agree with two previous theoretical studies on relaxed vacancies.[13,24] In the first study,[13] the electronic eigenvalues are located about 0.6 eV above the top of the valence band, with a slight raise in energy ($\approx$ 0.01 eV) for increasing charge on the vacancy and no loss of degeneracy. In the second study,[24] the vacancy occupancy levels,[4] as measured with respect to the top of the valence band, range from 0.19 eV for the $(0/-1)$ transition to 0.32 eV for the $(-2/-3)$ transition. The small change in the occupancy levels as estimated for different transitions (0.13 eV) agrees with that found from present results (0.044 eV). Anyway, the Ga vacancy behaves as a positive-U system. This result is related to the absence of sizable Jahn-Teller distortions for the

neutral and charged vacancies and suggests that there is no significant energy gain for the system in the presence of lattice distortions favoring an interaction between the As dangling bonds of the vacancy. A different behavior is shown when Si and Ga dangling bonds are involved, as in the case of V_{Si} in c-Si,[4] and of As vacancies in GaAs,[13] respectively. This could be accounted for by the fact that only in the case of the As dangling bonds the As atoms give rise to stable configurations. In those cases, indeed, they form three covalent bonds and carry electrons not involved in a chemical bond as, e.g., in the case of the arsine molecule.

B. Hydrogen-decorated Ga vacancies

1. Structural properties

The structure of a V_{Ga}^{-n} decorated with mH$_s$ (m = 1–4) has been investigated for the neutral (n = 0) and the negative charge states of the vacancy (n = 1–3). A configuration of the *neutral* vacancy with three H$_s$ is presented in Fig. 2(a). The formation of an As-H$_s$ bond induces a shift of the As atom in the [111] direction away from the vacancy, opposite to that found for the isolated vacancy. The As-H$_s$ bond length has a constant value of 1.55 Å in the cases of one to three H$_s$, and increases to 1.62 Å in the case of four H$_s$. A comparison with the As-H bond length in the arsine molecule, 1.52 Å,[25] suggests the formation of strong, stable bonds only when one to three H$_s$ decorate the vacancy. The stability of the As-H$_s$ bonds has been evaluated by calculating the dissociation energy (E_d) of one bond in the V_{Ga}^0–mH$_s$ complexes (m = 1–4). This quantity has been estimated as the energy difference between the initial and the final state of the reaction

$$[V_{Ga}^0 + m\mathrm{H}_s] \longrightarrow [V_{Ga}^0 + (m-1)\mathrm{H}_s] + \mathrm{H}^0,$$

where the H atom released by the complex is located in its site of minimum energy in GaAs.[26] The dissociation energies for the above processes, reported in the upper part of Table I, are given by

$$E_d = E[V_{Ga}^0 + (m-1)\mathrm{H}_s] + E[H^0] - E[V_{Ga}^0 + mH_s] - E[\mathrm{GaAs}],$$

where, e.g., $E[V_{Ga}^0$–mH$_s]$ is the total energy of a 32-atom supercell containing a neutral Ga vacancy plus mH$_s$. The first three H$_s$ are strongly bound to the As atoms, the fourth H$_s$ is weakly bound, thus making the V_{Ga}^0–4H$_s$ configuration barely stable. This result indicates that hydrogen saturators can form stable complexes with the neutral Ga vacancy *until their electrons fill empty levels of the vacancy* [see Fig. 2(b)], i.e., until the total number of electrons introduced into the vacancy equals that of the valence electrons removed together with the gallium atom.

Similar results hold also for the negatively charged-vacancy cases ($n \neq 0$). The As atoms, which are bound to the H atoms, relax away from the vacancy. The H$_s$s form stable As-H$_s$ bonds, with lengths comparable to the arsine ones, as far as they can accommodate their electrons in empty levels of the vacancy, i.e., for $m+n \leq 3$ (n = 1–3), as also shown by valence-charge-density plots in the (110) plane (not reported here). Otherwise, longer (and weaker) As-H$_s$ bonds are formed. In particular, the dissociation energies reported in the upper part of Table I show that the V_{Ga}^{-1}, V_{Ga}^{-2}, and V_{Ga}^{-3} form a weak bond with a third, second, and first H$_s$, respectively, in agreement with the trend found for the As-H$_s$ bond lengths.

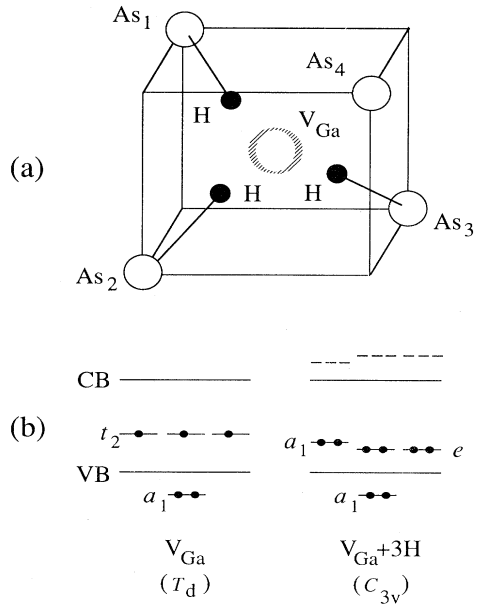

FIG. 2. (a) Scheme of an atomic configuration for a Ga vacancy V_{Ga} decorated by three H saturators; (b) schematic illustration of the electronic levels of a neutral Ga vacancy without H atoms (left side) or with three H saturators (right side).

2. Electronic structure of hydrogen-decorated Ga vacancies

The electronic structure of complexes formed by the *neutral* vacancy and three hydrogen saturators is qualitatively represented in Fig. 2(b). The structure of the isolated gallium vacancy is shown on the left side of Fig. 2(b), the bonding and antibonding levels due to interactions between the H$_s$ and the vacancy are shown on the right side of the same figure. The T_d symmetry of the isolated vacancy is reduced to C_{3v} and the threefold-degenerate t_2 level is split into a nondegenerate a_1 level and a twofold-degenerate e level. These levels accommodate the three H$_s$ electrons and correspond to bonding As-H$_s$ interactions. They are lower in energy with respect to the levels found in the isolated vacancy case, but still located in the energy gap (the a_1 and the e levels are 0.59 and 0.47 eV above the top of the valence band, respectively). An inspection of the charge densities $|\Psi_{n,\mathbf{k}}|^2$ corresponding to the As-H$_s$ antibonding levels [dashed lines in Fig. 2(b)] shows that the spare

TABLE I. Dissociation energy values of an As-H bond in complexes involving variously charged states of a gallium vacancy and several hydrogen atoms (see text). Three different cases are reported in the table, from the top to the bottom: (i) only $m\mathrm{H}_s$, hydrogen atoms saturating As dangling bonds; (ii) $m\mathrm{H}_s$ and one $\mathrm{H}^0_{\mathrm{BC}}$, a neutral H atom at a BC site next to the vacancy; (iii) $m\mathrm{H}_s$ and one $\mathrm{H}^+_{\mathrm{BC}}$, a proton at a BC site next to the vacancy. Dissociation energies are given in eV and refer to the breaking of a bond involving a H saturator in case (i), a $\mathrm{H}^0_{\mathrm{BC}}$ in case (ii), and a $\mathrm{H}^+_{\mathrm{BC}}$ in case (iii). In all cases, a neutral hydrogen atom is released.

Complex	H atoms	V_{Ga}^0	V_{Ga}^{-1}	V_{Ga}^{-2}	V_{Ga}^{-3}
$[V_{\mathrm{Ga}}^{-n} + m\mathrm{H}_s]$	H_s	-2.30	-2.14	-2.07	-0.25
	$2\mathrm{H}_s$	-2.10	-1.96	-0.20	
	$3\mathrm{H}_s$	-2.03	-0.26		
	$4\mathrm{H}_s$	-0.42			
$[V_{\mathrm{Ga}}^{-n} + m\mathrm{H}_s + \mathrm{H}^0_{\mathrm{BC}}]$	$\mathrm{H}^0_{\mathrm{BC}}$	-0.91	-0.81	-0.73	0.29
	$\mathrm{H}_s + \mathrm{H}^0_{\mathrm{BC}}$	-0.85	-0.71	0.42	0.50
	$2\mathrm{H}_s + \mathrm{H}^0_{\mathrm{BC}}$	-0.83	0.42	0.60	
	$3\mathrm{H}_s + \mathrm{H}^0_{\mathrm{BC}}$	0.44	0.30		
$[V_{\mathrm{Ga}}^{-n} + m\mathrm{H}_s + \mathrm{H}^+_{\mathrm{BC}}]$	$\mathrm{H}^+_{\mathrm{BC}}$		-0.91	-0.81	-0.73
	$\mathrm{H}_s + \mathrm{H}^+_{\mathrm{BC}}$		-0.85	-0.71	0.42
	$2\mathrm{H}_s + \mathrm{H}^+_{\mathrm{BC}}$		-0.83	0.42	
	$3\mathrm{H}_s + \mathrm{H}^+_{\mathrm{BC}}$		0.44		

electron of a fourth H_s in the vacancy should be accommodated in the conduction band, which justifies the low stability of the configuration with four H_s. Furthermore, when four H_s are inserted in the vacancy, the vacancy levels are higher in the energy gap than in the case of three H_s. Thus, the hydrogen saturators do not remove the vacancy levels from the energy gap, at least in the case of a neutral vacancy. This is likely due to the fact that H atoms may saturate As dangling bonds in the vacancy and restore the right number of electrons (e.g., the three electrons removed with the Ga atom) but they cannot fully reproduce the effects of four, partially ionic Ga-As bonds as they do instead for the Si-Si fully covalent bond in the case of the Si vacancy in crystalline silicon.[6] The same conclusions can be drawn on the basis of the results obtained in the case of *charged* vacancies: *The gallium vacancy is never passivated by the hydrogen saturators*, independently of its state of charge. Furthermore, whenever the vacancy levels are filled by the extra electrons of the charged vacancies and/or by the electrons of the H saturators, a further electron carried by a H atom must be accommodated in the conduction band, which leads to less stable complexes. This accounts for the relationship $m + n \leq 3$ ($n = 0$–3) previously found between the number m of the strong As-H_s bonds and the charge n of the vacancy in stable complexes.

Although the presence in the energy gap of states due to vacancy-hydrogen complexes may provide the final states involved in the radiative donor-acceptor-like transitions observed in hydrogenated GaAs, the H saturators do not provide the initial states (donor levels) involved in the same transitions. Therefore, different hydrogen locations in the lattice have to be investigated, in particular the bond center site where a hydrogen-atom nearest neighbor of a vacancy might maintain the donor character it has in a perfect crystal of GaAs.[26]

C. Hydrogen in a bond center next to a Ga vacancy

Let us consider first the complex formed by a *neutral* H_{BC} and a *neutral* V_{Ga} without hydrogen saturators, as shown in Fig. 3. The equilibrium geometry is obtained for Ga-H_{BC} and As-H_{BC} bond lengths equal to 1.74 Å and 1.66 Å, respectively. These values are in better agreement with those found for a H^+ at the BC site

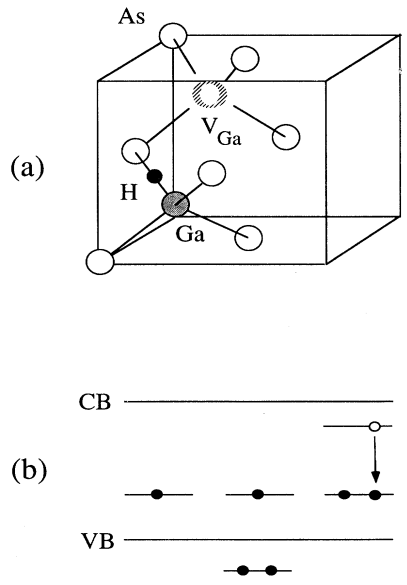

FIG. 3. (a) Scheme of an atomic configuration for a Ga vacancy V_{Ga} with a nearby H at a BC site (see the text); (b) schematic illustration of the electronic levels of the configuration shown in part (a).

in the perfect GaAs case (1.80 and 1.52 Å, respectively), than with those found for a H^0 at the same site (1.68 and 1.72 Å, respectively).[27] Indeed, the H atom is nearer to the As atom than to the Ga atom, while the presence of a nearby vacancy allows a greater relaxation of the As-Ga bond. These results can be understood when one considers the electronic levels corresponding to this configuration. An empty level related to the H atom is found in the energy gap, about 0.3 eV below the bottom of the conduction band, in addition to the defect levels of the vacancy, which gain one electron [see Fig. 3(b)]. Therefore, the H_{BC} looses its electron and remains as a proton in the bond center, where it maintains the donor-like nature exhibited in perfect GaAs. This is also manifested in the charge density plot of the H-defect-state wave function $|\Psi_{n,\mathbf{k}}|^2$, given in Fig. 4. Indeed, this charge density shows that the state induced by the H_{BC} is an antibonding combination of Ga and As p orbitals, which induces (i) a nodal plane on the H atom and (ii) a piling up of the charge density on the Ga and As atoms — two fingerprints of the H donor state.[27–29]

The above process may be modeled schematically by the reaction

$$[V_{Ga}^0] + H_{BC}^0 \rightarrow [V_{Ga}^{-1} + H_{BC}^+],$$

where the final product gives rise to the formation of a D-A pair. In the present case, the neutral charge state of the vacancy has been assumed as the stable one, i.e., the Fermi level is located above that of the V_{Ga}^0 (and below that of the V_{Ga}^{-1}). The charge -1 on the vacancy is therefore stabilized by the formation of the D-A pair. When the $[V_{Ga}^{-1} + H_{BC}^+]$ complex dissociates, the vacancy comes back to its initial neutral state and a neutral H atom is released

$$[V_{Ga}^{-1} + H_{BC}^+] \rightarrow [V_{Ga}^0] + H^0.$$

The corresponding dissociation energy, given by

$$E_d = E[V_{Ga}^0] + E[H^0] - E[V_{Ga}^{-1} + H_{BC}^+] - E[GaAs],$$

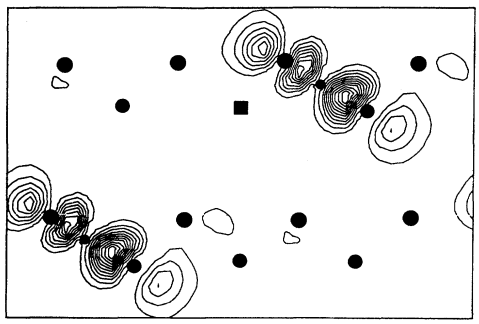

FIG. 4. Contour plots in the (110) plane of the charge density $|\Psi_{n,\mathbf{k}}|^2$ corresponding to the donor state induced by the H atom located at the BC site (see the text). The atomic positions are indicated by full dots, big for As atoms, medium for Ga atoms, and small for the H atoms. The Ga vacancy is represented by a full square.

is equal to -0.91 eV. (See the middle part of Table I, where the D-A complex is reported in terms of the initial components of the above reaction, $[V_{Ga}^0]$ and H_{BC}^0.)

A comparison with the dissociation energy of an As-H_s bond formed by a neutral H atom interacting with a neutral vacancy (-2.30 eV, see the upper part of Table I) shows that the H_{BC} atom forms a weaker bond than that formed by H_s. Correspondingly, a comparison between the total energies of the $[V_{Ga}^{-1} + H_{BC}^+]$ and the $[V_{Ga}^0 + H_s]$ complexes — which have the same total charge — shows that the D-A configuration is metastable with respect to that of the decorated vacancy: A neutral H atom tends therefore to saturate an As dangling bond of a neutral V_{Ga} in preference to be located at a bond center site.

Similar metastable configurations are obtained when one considers the complexes formed by a *neutral* H_{BC} and a nearby *charged* vacancy with no hydrogen saturators (fifth row of Table I). For instance, when the Fermi level position makes stable the charge state -1 of the vacancy, a V_{Ga}^{-1} and a H_{BC}^0 form a $[V_{Ga}^{-2} + H_{BC}^+]$ complex, which is metastable with respect to the $[V_{Ga}^{-1} + H_s]$ complex. Geometries, dissociation energies, and electronic configurations similar to those obtained in the case of a neutral vacancy case are found, *except* for the V_{Ga}^{-3} vacancy. In this case, the defect levels are fully occupied. The additional electron is localized on the H_{BC} atom and occupies the donor level. No D-A pair can be formed. The equilibrium geometry is similar to that found for the *neutral* H_{BC} in "perfect" GaAs. However, this configuration is unstable and exhibits a positive dissociation energy (0.29 eV).

In summary, if there is an empty defect level, the Coulomb interaction between the H_{BC}^+ and the charged vacancy stabilizes a D-A configuration where the vacancy has changed its charge state from $-n$ to $-(n+1)$. However, the D-A complexes are metastable with respect to the complexes where the H atoms saturate the As dangling bonds. If all the defect levels are full, the electron carried by the H atom goes instead in the donor state, higher in energy than the vacancy states, thus making the configuration unstable.

The decoration with m hydrogen saturators of a *neutral* vacancy interacting with a nearby H_{BC} does not appreciably change the above results, as shown by the dissociation energy of the As-H_{BC} bonds reported in the middle part of Table I.

The same considerations apply in the case of the decoration with m hydrogen saturators of a *charged* vacancy (n=1–3) interacting with a nearby H_{BC}. The complexes are metastable whenever $m+l+n \leq 3$, where l is the number of the H_{BC} atoms ($l = 1$), unstable for $m+l+n > 3$.[30]

Let us now consider a different case. A donor-acceptor pair may result also from the direct interaction between a *charged vacancy* and a diffusing *proton* localized at the BC site (H_{BC}^+). In this case, the dissociation of the proton-vacancy complexes into a neutral H atom and a charge vacancy implies the capture of one electron. In fact, if the Fermi level position makes the charge state $-n$ of the vacancy stable, the reaction of dissociation

$$[V_{Ga}^{-n} + H_{BC}^+] \rightarrow [V_{Ga}^{-n+1}] + H^0$$

must be followed by the capture of one electron to restore the initial charge state of the vacancy $-n$. (Alternatively, the H^+_{BC} ion may capture one electron before the complex dissociates.) If the electron capture is neglected, the dissociation energies relative to the above reaction are exactly the same concerning the dissociation of the $[V_{Ga}^{-n+1} + H^0_{BC}]$ complexes, as shown in the lower part of Table I. These dissociation energies are underestimated because the V_{Ga}^{-n} final configuration is expected to be higher in energy than the V_{Ga}^{-n+1} one. The stability of the configurations involving a proton at a BC site will be discussed in detail in the next section.

D. H_s vs H^+_{BC} stability

In the previous subsections, stable configurations have been found for mH_s-V_{Ga} complexes, metastable for H_{BC}-mH_s-V_{Ga} complexes. The dissociation energies found for H saturators are also systematically higher than those found for H_{BC} atoms, thus suggesting that neutral H atoms tend to decorate a vacancy instead of forming *D-A* pairs.

D-A pairs may also be formed by charged vacancies and protons located at BC sites. However, the stability of these *D-A* configurations with respect to those of H_s-decorated vacancies cannot be established by a direct comparison of the total energies of the complexes. In fact, for a given stable charge state of the vacancy, determined by the Fermi energy position, complexes with a different total charge have to be compared. As an example, the total energy of the $[V_{Ga}^{-1} + H_s]$ complex should be compared with that of the $[V_{Ga}^{-1} + H^+_{BC}]$ complex. The relative stability of configurations with different total charges has been therefore analyzed by comparing the dissociation energies of the $[V_{Ga}^{-n} + H^+_{BC}]$ complex given in the lower part of Table I (i.e., relative to a dissociation of the complex, which leaves the vacancy in the charge state $-n+1$) with those of the decorated vacancies, given in the upper part of the same table. Although the dissociation energies of the *D-A* configurations are likely to be underestimated, the marked differences between these dissociation energies and those of the decorated vacancies lead to quite clear conclusions. In the case of one or two H atoms interacting with a V_{Ga}^{-1}, a H saturator forms a stronger bond than a proton at the BC site, as obtained in the case of a neutral H at the BC site. On the contrary, in the case of three H atoms interacting with V_{Ga}^{-1} the third H saturator forms a weaker bond than a proton at the BC site, -0.26 eV instead of -0.83 eV. Similar results are obtained for complexes involving double or triple negatively charged vacancies, thus suggesting that the neutral H atoms interacting with a Ga vacancy tend to saturate the As dangling bonds whenever their total number k is smaller or equal to the number of the electrons which may be accommodated in the defect states ($k \leq 3-n$). For $k = (3-n)+1$, i.e., in the lack of empty defect states, a further H atom looses its electron and is located as a proton at a BC site next to the vacancy.

This result has been confirmed by a comparison between total-energy values which involves isolated charged vacancies used as reservoirs of electrons in the reaction

$$[V_{Ga}^{-n} + H^+_{BC} + mH_s] + [V_{Ga}^{-j-1}] \rightarrow [V_{Ga}^{-n} + (m+1)H_s] + [V_{Ga}^{-j}] ,$$

where the initial and final terms have the same total charge. The total-energy differences ΔE between the initial and final products are reported in Table II for $n = 1-3$, $m = 0-2$, and $j = 1, 2$. As an example, let us consider the case $n = 3$, $m = 0$, $j = 2$ (last row in the table)

$$[V_{Ga}^{-3} + H^+_{BC}] + [V_{Ga}^{-3}] \rightarrow [V_{Ga}^{-3} + H_s] + [V_{Ga}^{-2}].$$

The total-energy difference

$$\Delta E = E[V_{Ga}^{-3} + H^+_{BC}] + E[V_{Ga}^{-3}] - E[V_{Ga}^{-3} + H_s] - E[V_{Ga}^{-2}]$$

has a value equal to -0.48 eV. This negative value includes the difference in energy between the two different charged states of the isolated vacancy used as a reservoir of electrons, $E[V_{Ga}^{-3}] - E[V_{Ga}^{-2}]$, which has not been explicitly evaluated but can be safely assumed to be small and positive. Thus, the above ΔE value underestimates the stability of the $[V_{Ga}^{-3} + H^+_{BC}]$ complex and clearly indicates that the most stable configuration is obtained when a proton is located at the bond center site. The values of ΔE reported in Table II confirm the results obtained from the above discussion of the dissociation energies and show that the main contribution to ΔE comes from the differences in E_d reported in Table I ($-0.48 = -0.73 + 0.25$, in the example discussed above).

In summary, the interaction of k H atoms with a V_{Ga}^{-n} may lead to one of the following complexes:

$$[V_{Ga}^{-n} + kH_s], \quad (1)$$

$$[V_{Ga}^{-n} + (k-1)H_s + H^0_{BC}], \quad (2)$$

$$[V_{Ga}^{-n} + (k-1)H_s + H^+_{BC}]. \quad (3)$$

Depending on the relative values of k and n, different results are obtained: For $k \leq 3-n$, complexes (1) have the highest dissociation energies for the H atoms; for $k =$

TABLE II. Total-energy differences ΔE between complexes corresponding to the formation of a donor-acceptor pair where a proton is located at a BC site next to the vacancy (first column) and complexes formed by a charged Ga vacancy decorated by neutral H saturators (second column, see text). Negative values of ΔE indicate that the complex in the first column is more stable than the complex in the second column. All values are given in eV.

D-A complexes	Decorated vacancies	ΔE
$[V_{Ga}^{-1} + H^+_{BC}]$	$[V_{Ga}^{-1} + H_s]$	1.43
$[V_{Ga}^{-1} + H_s + H^+_{BC}]$	$[V_{Ga}^{-1} + 2\,H_s]$	1.14
$[V_{Ga}^{-1} + 2\,H_s + H^+_{BC}]$	$[V_{Ga}^{-1} + 3\,H_s]$	-0.67
$[V_{Ga}^{-2} + H^+_{BC}]$	$[V_{Ga}^{-2} + H_s]$	1.25
$[V_{Ga}^{-2} + H_s + H^+_{BC}]$	$[V_{Ga}^{-2} + 2\,H_s]$	-0.62
$[V_{Ga}^{-3} + H^+_{BC}]$	$[V_{Ga}^{-3} + H_s]$	-0.48

TABLE III. Theoretical estimates of the electronic eigenvalues for differing charges on the Ga vacancies, and their experimental counterparts. In the case of hydrogen-vacancy complexes (fifth row), the electronic eigenvalues have been obtained for stable configurations where a proton is located at a BC site next to a charged vacancy partially saturated with H atoms (see text). All values are given in eV.

Ref.		H	V_{Ga}^{-1}	V_{Ga}^{-2}	V_{Ga}^{-3}
11	unrelaxed	no	0.283	0.436	0.650
12	unrelaxed	no	0.250	0.390	0.570
13	relaxed	no	0.57	0.58	
Present work	relaxed	no	0.704	0.721	0.734
Present work	relaxed	yes	0.528	0.618	0.658
8	exp.	yes	0.355	0.475	0.545

$3 - n + 1$, complexes (1) easily dissociate, complexes (2) are unstable, while complexes (3) are stable.

E. Electronic levels of V_{Ga}-H_{BC} complexes and comparison with experimental results

The electronic eigenenergies corresponding to the isolated gallium vacancy levels are reported in the fourth row of Table III, as evaluated in the present work. Therein, one can also find the results obtained within a tight-binding approach[11] and a self-consistent semiempirical tight-binding technique,[12] in unrelaxed systems, and within a Car-Parrinello approach, in relaxed systems.[13]

In the absence of hydrogen atoms, the agreement between the present LDA results and the Car-Parrinello results[13] is quite good. In both cases, the electronic eigenenergies are almost constant for changes in the vacancy charge. The differences in the absolute values found in the two approaches at a given vacancy charge are likely to be due to the different pseudopotentials employed, which result in different values for the GaAs energy gap.[23] Much larger differences are found with respect to the tight-binding results,[11,12] where relaxation effects have not been taken into account. In this case, the electronic eigenenergies strongly increase for an increasing negative charge on the vacancy, while the values are on the average lower than those found in the present LDA and Car-Parrinello results.

When H atoms interact with gallium vacancies, the stable configurations giving rise to *D-A* pairs involve both H saturators and a positive H ion at the BC site, see Fig. 5(a). The electronic eigenenergies are lowered with respect to the isolated case as a consequence of the bonding interactions with the H saturators and split by a small amount due to the lower symmetry of the complex, as shown as an example in Fig. 5(b). In the fifth row of Table III, one can find the average values of these electronic eigenenergies for each value of the charge on the vacancy, in the sixth row one finds the values determined from PL measurements in hydrogenated *p*-type GaAs. Although the experimental values should be compared with the occupancy levels, not evaluated yet for H-decorated vacancies, they can be qualitatively compared also with present estimates of electronic eigenenergies. If the dependence on the charge of the vacancy of the eigenvalues given in Table III is considered, the trend of the present results is the closest to that of the experimental results (present and experimental values differ roughly by a constant, 0.14 ± 0.03 eV). This agreement suggests that the stable [V_{Ga}+H_{BC}] complexes discussed in the present work are the most likely responsible of the donor-acceptor-pair transitions reported in hydrogenated GaAs.

The interaction of H atoms with Ga vacancies can therefore be summarized as in the following. When H atoms are introduced into a slightly *p*-type GaAs lattice, they tend to be located at the BC sites thus giving rise to a deep donor level in the energy gap.[27] This leads to the compensation of the Ga vacancies and to the formation of H^+ ions. H^+ ions and neutral H atoms diffuse into the lattice and form pairs with the vacancies by starting to saturate the As-dangling bonds and to fill the empty energy levels of the vacancy. The number of the H saturators strongly bound to a vacancy depends on the charge state of the vacancy. After all the vacancy levels have

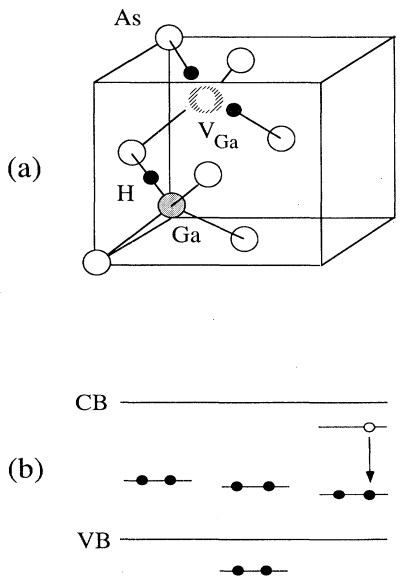

FIG. 5. (a) Scheme of an atomic configuration for a Ga vacancy V_{Ga} decorated by two H atoms, with a nearby H at a BC site (see the text); (b) schematic illustration of the electronic levels of the configuration shown in part (a).

been filled, stable complexes can be formed by a further proton located at a BC site near the vacancy. The inhomogeneity in the H distribution depth typical of the hydrogenation process gives rise to a coexistence in the same sample of different charge states of the Ga vacancy. These states and the corresponding complexes formed by the ionized H donors may account for the donor-acceptor-like transitions reported as a function of the excitation power in hydrogenated GaAs.[8]

IV. CONCLUSIONS

The interaction of atomic hydrogen with Ga vacancies has been investigated in a first-principles LDA approach. The H atoms tend to saturate the As dangling bonds in the vacancy by forming strong As-H_s bonds until the vacancy levels are thoroughly filled. Further stable complexes can be formed where a H^+ ion is located at a BC site next to a charged, fully saturated vacancy. In these configurations, a donor level is introduced in the energy gap. The energy of the vacancy levels is slightly affected by hydrogenation and remains located in the energy gap contrary to what has been reported for other deep and shallow defects. The H^+_{BC} ion and the charged vacancy can then give rise to the donor-acceptor-pair transitions experimentally observed in hydrogenated slightly p-type GaAs. A satisfactory agreement has been found between the electronic eigenvalues corresponding to the vacancy levels in these complexes and the electronic levels determined from photoluminescence measurements.

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