Structure, kinetics, and passivation of hydrogen-acceptor complexes in gallium arsenide: A theoretical study

Aldo Amore Bonapasta[*]

Consiglio Nazionale delle Ricerche-Istituto di Chimica dei Materiali (ICMAT), Via Salaria Km 29.500, CP-10, I-00016 Monterotondo Scalo, Italy

Mario Capizzi

Istituto Nazionale Di Fisica Della Materia, Dipartimento di Fisica, Università di Roma (La Sapienza), Piazzale A. Moro 2, I-00185 Roma, Italy

Paolo Giannozzi

Istituto Nazionale Di Fisica Della Materia, Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

The structure, reorientation kinetics, and passivation mechanism of complexes formed by a H atom and As-site or Ga-site acceptors, e.g., the Si_{As}-H-Ga and the Zn_{Ga}-H-As complexes in GaAs, have been investigated by first-principles local-density-functional methods. In both complexes, the stable configuration is found for the H atom located at a bond-centered site. The H atom is bound to the Si acceptor in the Si_{As}-H-Ga complex and to the As atom in the Zn_{Ga}-H-As complex. In spite of the different H bonds, similar vibrational properties and reorientation kinetics have been theoretically found for the two complexes. The present calculations well reproduce the experimental values of the vibrational frequencies and of the complex dissociation energies, as well as account for the acceptor passivation. A good agreement is also found with the reorientation energy of the Si_{As}-H-Ga complex, while the unusually high relaxation rates of the Zn_{Ga}-H-As complex measured by anelastic-relaxation investigations remains unexplained. In fact, neither the energy barrier estimated for the complex reorientation nor two different tunneling models account for those high relaxation rates. [S0163-1829(98)00220-3]

I. INTRODUCTION

The passivation after hydrogenation of shallow and deep impurities in semiconductors is deeply related to the microscopic properties of the complexes formed by the H atom and the impurities.[1] Infrared-absorption (IR) spectroscopy provides an important tool for investigating the microscopic structure of those complexes. In the case of shallow dopants, the study of the localized vibrational modes (LVM's) of the hydrogen atoms allows us to identify the H-X bonds involved in the complex, where X is the dopant or one of its nearest neighbors. A uniaxial stress may lift energy-level degeneracies and induce frequency shifts, which provide indications of the symmetry of the complex and of the location of the H atom.[2,3] Furthermore, when a H atom is located next to a bond-centered site (BC), see Fig. 1, a stress-induced-alignments technique allows us to investigate the H motion around the dopant atoms.[2,4–7] As an example, Fig. 2(a) shows the *off-axis* BC configuration of the complex formed in GaAs by the H atom and a Si acceptor located at an As site (Si_{As}). In this configuration, the H atom is next to the BC site of a Si_{As}-Ga bond, *off* the bond axis. A possible motion of the H atom around the acceptor is shown in the figure by a circular path from an *off-axis* BC site to the *off-axis* BC site of a neighboring Si_{As}-Ga bond. The BC configuration of the H complex has a trigonal symmetry and the four equivalent threefold axes are directed along any of the [111] crystal axes.[8] The complex may reorient, therefore, among its four possible orientations by thermally assisted H jumps over a potential barrier. A uniaxial stress lowers the

symmetry of the crystal and can make complexes with different orientations inequivalent. Since this lifts the degeneracy of the ground state of the complex, it is possible to measure the kinetics of the H motion and to determine the barrier height between differently oriented complex configurations. If the stress is applied, indeed, at high temperature, the complexes reorient and the different states will be popu-
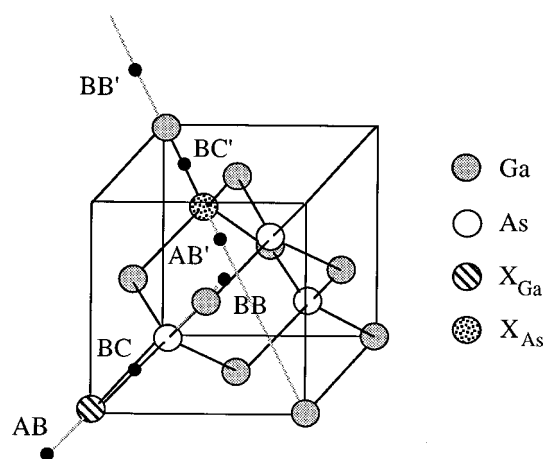

FIG. 1. GaAs unit cell showing the Ga site (X_{Ga}) and As site (X_{As}). The high-simmetry interstitial hydrogen sites investigated in the present work are also indicated. BC is the bond-centered site corresponding to the As-X_{Ga} bond. AB and BB are the antibonding and back-bonded sites on the dopant X_{Ga} side and on the arsenic side, respectively, for the same bond. Primes identify the corresponding hydrogen sites relative to the X_{As}-Ga bonds (see the text).
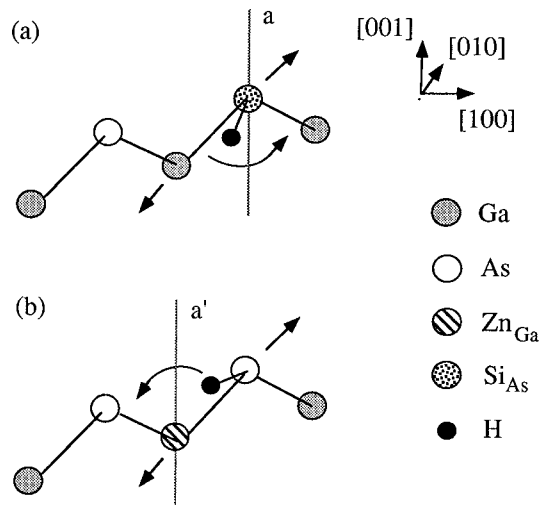
FIG. 2. *Off-axis* bond center configuration for (a) the Si_{As}-H_{BC}-Ga and (b) the Zn_{Ga}-H_{BC}-As complexes. The arrows indicate the atomic displacements with respect to the unrelaxed positions and a circular path for the H motion around the acceptor atom.

TABLE I. Experimental H stretching frequencies, ν_s, and activation energies for the H-complex reorientation, E_a, are given in the upper part of the table for different H-acceptor complexes in Si and GaAs. Experimental values for the stretching frequencies of H bonds in different simple molecules (complex molecules) are reported in the lower part of the table. Activation energies and stretching frequencies are given in eV and cm^{-1}, respectively.

Complex and/or Molecule	Bond	ν_s	E_a	Refs.
Si:B-H	Si-H-B	1903	0.19–0.22	5 and 9
GaAs:C_{As}-H	C-H	2635	0.50	3 and 7
GaAs:Si_{As}-H	Si-H	2095	0.26	3 and 7
GaAs:Be_{Ga}-H	As-H	2037	0.37	3 and 7
GaAs:Zn_{Ga}-H	As-H	2147	0.037[a]	3 and 14
CH_4	C-H	2917		12
SiH_4	Si-H	2187		12
AsH_3	As-H	2116		12
Zn-H	Zn-H	1608		13
(Ga-H)	Ga-H	1808		3

[a]In deuterated GaAs:Zn, see Ref. 14.

lated according to their Boltzmann factors, which gives rise to a net alignment of the complexes. The ensuing anisotropy in the polarized optical absorption as well as the splitting into components of the H-stretching band allows us to determine the symmetry of the center.[4,5,7] If a sample is cooled to a low temperature while the stress is maintained, the alignment can be frozen in and will persist until the stress is removed. When the sample temperature is increased, the H complexes reorient randomly among their equivalent configurations. Thus, measurements of the dichroism decay time at different T's allow us to estimate both the activation energy (E_a) and the rates for the complex reorientation. It has to be mentioned that such reorientation processes cannot be observed for H atoms located at antibonding (AB) or backbonded (BB) sites, see Fig. 1, where the effect of an applied stress is much smaller.[4]

The activation energies E_a have been generally estimated by IR spectroscopy measurements by assuming that the reorientation mechanism is a thermally activated process that involves single jumps over a barrier and can be described by an Arrhenius formula. More sophisticated mechanisms have been proposed, however, in the case of the B-H complex in crystalline silicon (c-Si). Here, measurements of the jump rates performed at high temperatures (≈ 120 K) by anelastic relaxation (AR) (Ref. 9) and at low temperatures (≈ 60 K) by IR techniques[10] have shown a deviation from the Arrhenius behavior. This behavior has been accounted for within the Flynn-Stoneham thermally assisted tunneling model.[10,11]

The results of IR and AR investigations[3,5,7,9,12–14] of different H-acceptor complexes in c-Si and c-GaAs are reported in Table I and Fig. 3. Table I gives the values of the H stretching frequencies ν_s, the H-X bonds involved in those vibrations, and the activation energies E_a for the reorientation process of the H complexes. The corresponding relaxation rates (or reorientation rates) are given in Fig. 3 for both hydrogen and deuterium complexes. In the case of the Zn acceptor in GaAs, the values of the H-complex activation energy and relaxation rates have been obtained by AR measurements.[14] The values of the stretching frequencies,

activation energies,[15,16] and of the parameters describing the effects of the stress on the H frequencies[7] (not reported in the table) are similar for all the complexes reported in Table I, except for the activation energy of the H complex in GaAs:Zn. Those same complexes are also characterized by similar values of the relaxation rates for temperatures ranging from 70 K to 120 K, see Fig. 3, which is quite surprising, especially in the case of the Be_{Ga}-H and Si_{As}-H complexes. In fact, the comparison of the H stretching frequencies with those of D, for the former complex,[17] and with the frequencies measured for molecular H-X bonds, for the latter complex (see Table I), suggests different H local bondings in those two complexes. In particular, that comparison and theoretical calculations[18,19] show that the H atom is bonded to the acceptor, in the case of As-site acceptors, and to one of the As atom's nearest neighbors of the acceptor, in the case of Ga-site acceptors.

In the case of the Zn_{Ga}-H complex, the IR investigations give only the hydrogen LVM's whose comparison with molecular H-X frequencies (see Table I) suggests the formation of a H-As bond, as in the case of Be_{Ga}. Recently, AR inves-

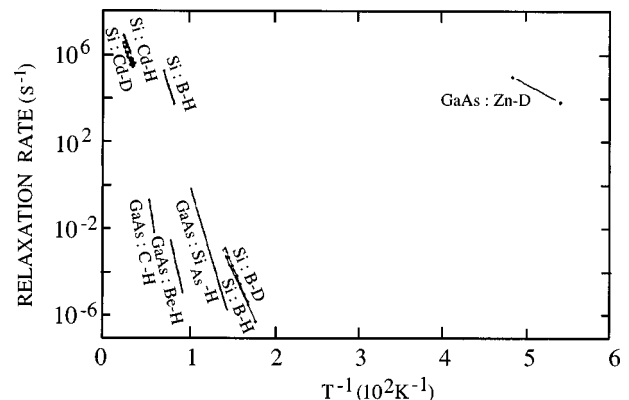FIG. 3. Experimental relaxation rates of different H- and D-acceptor complexes in c-Si and c-GaAs. The figure is taken from Ref. 14, with permission.

tigations in deuterated GaAs:Zn (Ref. 14) have measured high relaxation rates of the D complexes[20] at 20 K, and no relaxation rate at higher temperatures, see Fig. 3. These low-T relaxation rates differ sizably from those of the other complexes, both in magnitude and temperature dependence. The activation energy for the complex reorientation is very low, 37 meV, if one interpolates the relaxation rate values by an Arrhenius law, which, however, does not reproduce satisfactorily the elastic-energy-loss line shape without unphysical assumptions. The elastic-energy-loss curves are fitted, instead, by the thermally assisted tunneling model of Flynn and Stoneham.[11] In this case the coincidence energy, a characteristic parameter entering the model, turns out to be quite low, 34 meV.[14] Finally, it has to be mentioned that the absence of a complex reorientation at high T is quite surprising because the H local bonding in the Zn_{Ga}-H complex should be similar to that of the Be_{Ga}-H complex, which reorients at 120 K with an activation energy of 0.37 eV.

The aim of this work is to account for the similar vibrational properties experimentally found for As-site and Ga-site acceptors and for the very low E_a value found for the activation energy in the reorientation of the Zn_{Ga}-H complex. In the present paper, first-principle calculations have been performed to investigate the geometry, the chemical bonding, the hydrogen LVM's, and the reorientation of the Si_{As}-H and Zn_{Ga}-H complexes. The Be_{Ga}-H complex has not been considered since IR results suggest that its structure and vibrational properties are quite similar to those of the Zn_{Ga}-H complex.

In the case of the Zn_{Ga}-H complex, the present results support the structure suggested for this complex by IR results and account for their likeness to those found in the Be_{Ga}-H complex, thus confirming that Zn impurity is a good prototype of Ga-site acceptors. For both the Si_{As}-H and Zn_{Ga}-H complexes, a good agreement is found with the stretching frequencies and the dissociation energies of the H-Si_{As} and the H-As bonds. Moreover, the details of the geometry and of the chemical bonding, as well as the energies of the hydrogen LVM's, account for the likeness reported in the experimental results for the complexes involving As-site and Ga-site acceptors.[7] Likewise, the results concerning the complex reorientation indicate that the Si_{As}-H and the Zn_{Ga}-H complexes have similar dynamic behaviors and comparable activation energies for the H motion. Therefore, at high temperatures (70–120 K) the Zn_{Ga}-H complex should reorient with a thermally activated mechanism, as observed for the Si_{As}-H complex. As mentioned above, AR measurements do not give evidence, instead, of such a process, while the present results do not account for the high relaxation rates measured for the Zn_{Ga}-H complex. Since the AR results have been tentatively related to some kind of tunneling, reorientation mechanisms based on two tunneling models, the thermally assisted tunneling model[11] and a tunneling model involving excited vibrational states,[21] have been investigated. Unfortunately, neither model accounts for those high relaxation rates nor for their dependence on temperature, which should be likely related to a complex involving further defects or impurities in addition to the H and Zn atoms.

Finally, the present results show that the acceptor is passivated for both the Si_{As}-H and Zn_{Ga}-H complexes in their stable configurations.

II. METHODS

The equilibrium geometries of the Si_{As}-H and the Zn_{Ga}-H complexes have been investigated by *ab initio* total energy and atomic force calculations in the local-density-functional (LDF) framework and in the supercell approach.[22,23] The geometry of supercells containing the H and the acceptor atoms has been fully relaxed by minimizing the Hellmann-Feynman forces on the atoms.[24] The exchange-correlation functional of Ceperley-Alder[25] has been used together with norm-conserving pseudopotentials and plane-wave basis sets; **k**-space integration has been performed with the use of the special-points technique.[26] Separable *ab initio* pseudopotentials have been used in the case of Ga, As, and Si atoms.[27] In the case of Zn and H atoms, the pseudopotentials employed have been successfully used for the evaluation of phonons in II-VI semiconductors[28] and for the investigation of the H properties in GaAs, respectively.[29] The atomic pseudopotentials have been tested by investigating the structural and electronic properties of bulk materials and small molecules with different kinetic energy cutoffs. Reasonable values have been obtained by using kinetic energy cutoffs of 18–22 Ry. These energy cutoffs lead to lattice constants that approach their experimental counterparts within 1%, in the cases of the bulk GaAs and Si, within 3%, in the case of metallic Zn. They also lead to a direct energy gap of 1.39 eV for bulk GaAs.[30] The investigation of the SiH_4 and AsH_3 molecular geometries has given Si-H and As-H bond lengths of 1.43 Å and 1.48 Å, respectively, in good agreement with experimental results.[12]

The hydrogen vibrational frequencies in molecules and in complexes involving the acceptor atoms have been evaluated in the harmonic approximation. One H atom is moved away from its equilibrium position while the other atoms of the molecule (or of the supercell) are frozen in the positions of the minimum energy configuration (namely, it is assumed that the H motion is independent of that of the other atoms). The frequencies of the hydrogen LVM's have then been estimated by fitting to a parabola the total energy values corresponding to the different H positions. This procedure has been used successfully in the case of complexes formed by hydrogen and shallow defects in c-Si (Refs. 31 and 32) and c-GaAs.[16,18] As an example, in the case of the SiH_4 molecules, this procedure gives a H stretching frequency of 2110 cm^{-1} with a kinetic energy cutoff of 18 Ry, in good agreement with the experimental value of 2187 cm^{-1} reported in Ref. 12.

In the complexes involving Si or Zn acceptors, the dissociation energy of the bonds formed by the hydrogen atom has been estimated as the energy difference between the initial and the final state of the reactions

$$(Si_{As}\text{-H}) \rightarrow Si_{As} + H^0,$$

$$(Zn_{Ga}\text{-H}) \rightarrow Zn_{Ga} + H^0.$$
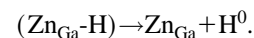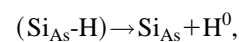
The H atoms released by the complexes are located in their minimum energy sites in GaAs.[29]

The dissociation energies are, respectively,

$$E_d = E(Si_{As}) + E(H^0) - E(Si_{As}\text{-H}) - E(GaAs),$$

TABLE II. Equilibrium geometries of the stable *off-axis* configurations of the Si_{As}-H_{BC}-Ga and Zn_{Ga}-H_{BC}-As complexes are given in the first and second row, respectively. The metastable configurations, *on-axis* BC for the Si_{As}-H_{BC}-Ga complex and BB for the Zn_{Ga}-H_{BC}-As complex, are given in the third and fourth row, respectively. ΔX and ΔY are the displacements of the X and Y atoms from the unrelaxed positions. θ is the bond angle between the As-Zn and the As-H bonds, in the Zn_{Ga}-H-As complex, and between the Si_{As}-Ga and the Si_{As}-H bonds, in the Si_{As}-H-Ga complex. d is the distance of the H atom from the X-Y bond. E_d is the dissociation energy of the H-Y bond and E_a is the activation energy for the complex reorientation. ν_s and ν_b are the stretching and bending frequencies of the H bonds, respectively. Atomic distances, energies and vibrational frequencies are given in Å, eV, and cm^{-1}, respectively.

X	Y	X-Y	ΔX	ΔY	H-X	H-Y	θ	d	E_d	E_a	ν_s	ν_b
Ga	Si_{As}	3.04	0.34	0.29	1.69	1.56	21.7	0.58	2.0	0.17	2000	880
Zn_{Ga}	As	3.21	0.49	0.32	1.74	1.54	12.3	0.32	1.6	0.21	2155	540
Ga	Si_{As}	3.23	0.45	0.37	1.66	1.57	0.0	0.0	1.9		2170	
Zn_{Ga}	As	2.92	0.24	0.27		1.55			1.14		1935	525

$$E_d = E(Zn_{Ga}) + E(H^0) - E(Zn_{Ga}\text{-}H) - E(GaAs),$$

where, e.g., $E(Si_{As})$ is the total energy of a 32-atom supercell containing a Si_{As} acceptor.

In the case of supercell calculations, convergence tests have been performed on the structural and electronic properties of the H complexes by using kinetic-energy cutoffs ranging from 16 to 22 Ry, supercells of 32 and 64 atoms, and **k**-point meshes equivalent to the (4,4,4) and (8,8,8) Monkhorst-Pack meshes in the zinc-blende unit cell. A reasonable convergence of the calculated values has been obtained by using 32-atom supercells, the (4,4,4) **k**-point mesh, and cutoffs of 18 or 22 Ry.

The hydrogen passivation of shallow impurities leads to the disappearance of the impurity levels from the energy gap. In the case of shallow donors, e.g., P in c-Si,[33] an estimate of the energy position of the electronic levels has been obtained by taking a weighted average of the electronic eigenvalues over several high symmetry points in the Brillouin zone. This procedure has clearly shown that the defect level deepens into the valence band when the H-P complex is formed.[33] On the contrary, in the case of acceptors like C_{As} in c-GaAs it is difficult to observe the electronic level of the isolated acceptor because this level is substantially degenerate with the top of the valence band.[16] In the case of Si_{As} and Zn_{Ga} acceptors, their electrical neutralization has therefore been investigated by analyzing the distribution of the electronic charge density $|\Psi_{n,\mathbf{k}}|^2$, which is given by the wave functions $\Psi_{n,\mathbf{k}}$ related to the defect level and to the states near the top of the valence band. A similar procedure has already been successfully applied in the case of the C_{As} acceptor.[16]

Finally, a Gaussian broadening scheme[34] has been used to deal with the Fermi surface, whenever the unit cell contained an odd number of electrons. Further details on the theoretical methods can be found in Ref. 16.

III. RESULTS AND DISCUSSION

A. Structural and electronic properties of the Si_{As}-H and the Zn_{Ga}-H complexes.

In the case of the complex formed by the silicon acceptor and hydrogen, three different configurations have been considered, with the H atom located at the BC, AB, or BB site (see Fig. 1). All these configurations have the trigonal sym-

metry indicated by IR measurements.[7] The BC configuration is the stable one, provided the H atom is *off* the Si_{As}-Ga bond. The *on-axis* BC configuration is metastable and 0.03 eV higher in energy. The AB and BB configurations are even higher in energy.[35] Details of the equilibrium geometries of the stable *off-* and the metastable *on-axis* BC configurations are given, respectively, in the first and third row of Table II. In the stable configuration, hereafter referred to as the Si_{As}-H_{BC}-Ga one, the H-Si bond is slightly perturbed by the presence of the neighboring Ga atom, as shown by the plot of the total (valence) charge density given in Fig. 4(a). This bonding is confirmed by the H-Si and H-Ga bond lengths, 5% and 7% greater, respectively, than those estimated by using the atomic covalent radii.[36] The estimates of the dissociation energy of the H-Si bond, 1.96 eV, and of the H stretching frequency, 2002 cm^{-1}, are in good agreement, respectively, with a previous theoretical estimate (1.75 eV, see Ref. 18) and a measured value (2095 cm^{-1}, see Ref. 7).

The BC, AB, and BB configurations have been investigated also in the case of the Zn_{Ga}-H complex. Once more, the *off-axis* BC configuration (i.e., the Zn_{Ga}-H_{BC}-As one) is the stable one. The AB configuration is unstable, while the BB configuration is metastable, 0.46 eV higher in energy than the stable configuration. The geometrical parameters of
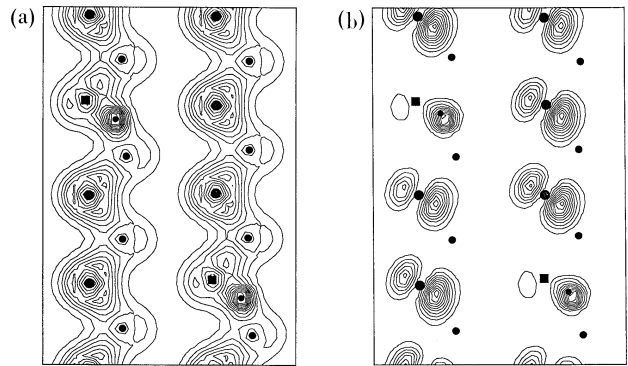

FIG. 4. Contour plots, in the (110) plane, of electronic charge densities corresponding to the Si_{As}-H_{BC}-Ga complex (see the text): (a) total (valence) charge density; (b) charge density as given by the $|\Psi_{n,\mathbf{k}}|^2$ function, which corresponds to an electronic level deep in the valence band. The atomic positions are indicated by a solid square for the Si_{As} acceptor and by solid circles of increasing size for the H, Ga and As atoms, respectively.

FIG. 5. Contour plots, in the (110) plane, of electronic charge densities corresponding to the Zn_{Ga}-H_{BC}-As complex (see the text): (a) total (valence) charge density; (b) charge density given by the $|\Psi_{n,\mathbf{k}}|^2$ function, which corresponds to an electronic level deep in the valence band. The atomic positions are indicated by a solid square for the Zn_{Ga} acceptor and by solid circles of increasing size for the H, Ga, and As atoms, respectively.
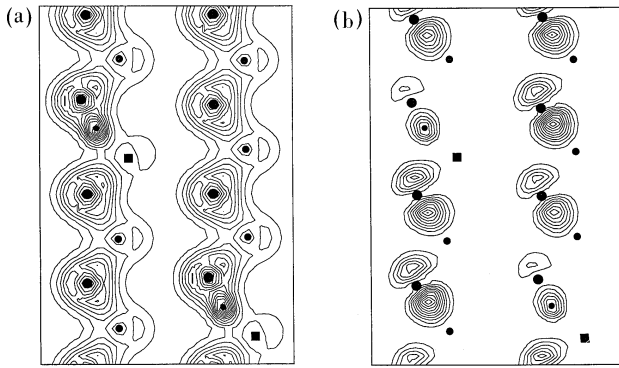
the stable BC and metastable BB configurations are given, respectively, in the second and fourth row of Table II. In the stable configuration, the H atom is mainly bonded to the As atom of the Zn_{Ga}-As bond involved in the complex. The H-As bond is slightly perturbed by the Zn acceptor, as shown by the distribution of the valence charge density given in Fig. 5(a). This is confirmed by the H-As and H-Zn bond lengths, 3% and 6% greater, respectively, than those estimated by using the atomic covalent radii.[36] The dissociation energy (1.6 eV) and the H stretching frequency (2156 cm^{-1}) evaluated for the H-As bond in the complex agree very well with their experimental counterparts, 1.6 eV and 2147 cm^{-1},[3] respectively. On the contrary, the values found for the metastable BB configuration are quite a bit lower than the experimental values. Thus, the present results support the IR studies, which suggest that the Zn_{Ga}-H complex has a BC stable configuration, as the Be_{Ga}-H complex does, and that the H stretching frequency is due to the H-As bond involved in the complex.[3]

In summary, the H atom is bonded to the Si_{As} acceptor in the Si_{As}-H_{BC}-Ga complex and to the nearest neighbor As in the Zn_{Ga}-H_{BC}-As complex. Nevertheless, a comparison between the structural properties of the two complexes shows that H has *quite similar local bondings* in the two cases. H is located at an *off-axis* BC site in both complexes and forms stable H-Si and H-As bonds that have comparable bond lengths, dissociation energies, and stretching frequencies. Furthermore, quite similar distributions of the electronic charge densities around the H atom are shown in Figs. 4(a) and 5(a) for the two complexes.

For what concerns the acceptor passivation, it should be taken into account that a hydrogen atom induces a donor level in the band gap of GaAs when placed in a bond-center site of a Ga-As bond.[29] H may therefore compensate for a shallow acceptor level by leading to the formation of H$^+$ ions and negatively charged acceptors. The electrical neutralization of the acceptor activity is achieved when the pairing between the mobile H ions and the ionized acceptors is accompanied by the disappearance of the defect level from the energy gap. This phenomenon is related to significant changes in the acceptor chemical bonding due to the forma-

tion of new bonds that generally involve the H atom, the acceptor atom, and its nearest neighbors. In the case of isolated Si_{As} and Zn_{Ga} acceptors, an analysis of the electronic eigenvalues shows that the acceptor level is already degenerate with the top of the valence band, as in the case of the C_{As} acceptor in c-GaAs.[16] This result does not allow us to relate a disappearance of the acceptor level in the gap to the effects of the hydrogen-acceptor interaction. The passivation of Si_{As} and Zn_{Ga} acceptors has been investigated, therefore, by analyzing the distribution of the total (valence) charge density and of the charge densities $|\Psi_{n,\mathbf{k}}|^2$, where the electronic wave function $\Psi_{n,\mathbf{k}}$ is related to the levels near the top of the valence band. In the absence of hydrogen, a plot of the $|\Psi_{n,\mathbf{k}}|^2$ function corresponding to the level at the top of the valence band (not shown here) indicates that this level is related to the p orbitals of the Si (or Zn) and As atoms, accordingly with the degeneracy found for the acceptor level with the levels at the top of the valence band. When the Si_{As}-H_{BC}-Ga complex is formed, the level at the top of the valence band is still related to the p orbitals of the As and acceptor atoms. However, the electronic level whose wave function *piles up* electronic charge between the H and Si_{As} atoms is now deep in the valence band; compare Fig. 4(b) with Fig. 4(a). The position of the level and the distribution of the related electronic charge accounts for the acceptor neutralization. A similar result is found in the case of the Zn_{Ga}-H_{BC}-As complex, where an electronic level deep in the valence band is related to a wave function piling up electronic charge between the H and the As atoms; compare Fig. 5(b) with Fig. 5(a).

The plots of the valence charge densities given in Figs. 4 and 5 and the structural properties of the H-Si and H-Zn complexes discussed above indicate that the bonds formed by the H atoms induce significant changes in the acceptor local bonding. It may be worth noticing that the acceptor passivation is achieved when the atoms in the complex recover their "natural" valence. In the Si_{As}-H_{BC}-Ga complex, the four sp^3 atomic orbitals of Si are involved in the formation of one strong H-Si bond and of three Ga-Si bonds, see Fig. 4(a), thus leading to the valence of 4 of the Si atom. The Ga atom in the complex slightly interacts with the H atom and has its "natural" valence of 3. In the Zn_{Ga}-H_{BC}-As complex, the H atom saturates the As atom, see Fig. 5(a), the Zn atom forms two equivalent bonds with two As neighbors, while the fourth As nearest neighbor of Zn has the valence of 5.

B. Reorientation kinetics of the Si_{As}-H and the Zn_{Ga}-H complexes

When a H atom migrates from a BC site to an equivalent site of an adjacent bond (i.e., the H complex reorientates), the chemical bonds involving the H atom rearrange and the lattice undergoes a large relaxation. This implies a relevant role of the vibrational modes of the heavy, host atoms as well as of the hydrogen high reactivity in the migration process. At low temperatures, the energy barrier for the H migration is generally estimated by performing static calculations where the total energy of different configurations of the H and host atoms is evaluated. Two different criteria have been used in previous works in order to select a limited num-

ber of configurations among the possible (infinite) ones. In the former case, the host atoms are fixed in different configurations chosen among those favored by the vibrational motions of those atoms. The optimum position of the H atom for each host configuration is then established by minimizing the total energy. In this case, one assumes that the H atom first waits for a configuration where the bond between the host atoms elongates and then follows the motion of the heavier atoms by moving to the BC site of the elongated bond (i.e., H waits for ''the opening of a door'').[37,38] Thus, one assumes that the most likely path for the H migration, which does not necessarily coincide with the minimum energy path, is that favored by the motion of the heavy atoms. However, this approach neglects the response of the host atoms to the presence of the H atom because it puts constraints on the motion of the host atoms. In the latter case, the H atom is fixed at different locations along a selected path, whereas the host lattice is able to relax. This approach provides a different way of sampling the configurations involving the H and host atoms, which are then investigated in order to find the minimum energy path for the H migration. Therewith, one assumes that the most likely path is the minimum energy one and that the configuration related to the minimum energy barrier is achieved in the real H migration as a consequence of the vibrational motions of the heavier atoms and of their interaction with H.

The first approach neglects the H-lattice interaction and may lead to an overestimate of the observed barrier height. The second approach, on the other hand, may overemphasize the response of the host atoms to the presence of H, thus leading to an underestimate of the experimental value. As a matter of fact, both approaches have been followed in the literature. DeLeo *et al.* have used the first approach in order to determine the barrier for H migration in undoped, intrinsic Si.[37] Those authors estimate a barrier $\lesssim 1$ eV, which has no experimental counterpart. Denteneer *et al.* have used, instead, the second approach in order to determine the barrier for the reorientation of the B-H_{BC}-Si complex in Si:B.[31] Those authors obtain a quite low value, 0.2 eV, in very good agreement with the experimental results (0.176 eV).[10]

In the present work, the latter approach has been used. The minimum energy path for the H motion has been estimated by moving the H atom along different, selected paths and by relaxing the supercell structure for each position of the H atom. This approach has been chosen for the following reasons: (i) In the presence of a substitutional impurity, it is difficult to set constraints on the motion of the heavier atoms because the presence of the impurity atom leads to a more complex vibrational behavior of the host atoms. (ii) It is possible to exploit the lattice symmetry in order to select the H paths. (iii) It is possible to take into account the interaction between the H and the host atoms, whose relaxation may depend on H location (in the converse choice the H atom passively follows the motion of the heavier lattice atoms). (iv) Finally, the chosen approach has produced a value for the barrier in good agreement with experiment in Si:B, where a H located at a BC site next to a shallow acceptor was involved, as in the present case.

In the case of the Zn_{Ga}-H_{BC}-As complex, a circular path in the (110) plane from the BC equilibrium site toward an equivalent BC site of a neighboring Zn_{Ga}-As bond has been
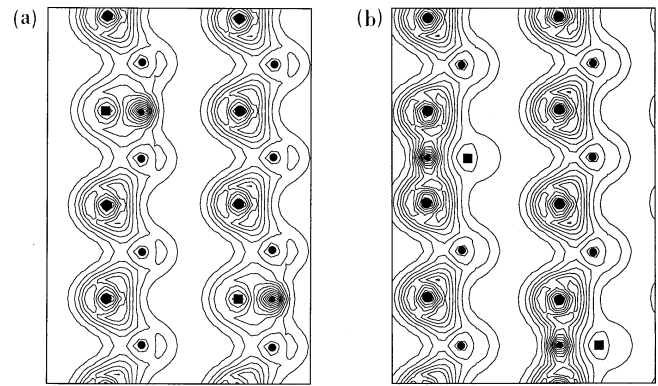

FIG. 6. Contour plots, in the (110) plane, of the total (valence) charge density in the case of the minimum energy barrier configurations of the complexes investigated in the present work (see the text): (a) Si_{As}-H_{BC}-Ga complex; (b) Zn_{Ga}-H_{BC}-As complex. The atomic positions are indicated by solid squares for the acceptor atoms and by solid circles of increasing size for the H, Ga, and As atoms, respectively.

considered first, see Fig. 2(b). In this case, the H-Zn distance has been kept almost constant during the H motion. Then, paths with different H-Zn distances have been considered in order to allow the Zn atom to relax in different ways. Since hydrogen locations off the (110) plane have been found to correspond to higher energies, H paths in the (110) plane turn out to be the most favorable ones. Therein, the total energy reaches a maximum when the H atom is midway between the two BC sites at the beginning and at the end of the chosen path. For symmetry reasons, this location is on the [001] axis passing through the position of the Zn atom in the unrelaxed lattice, namely the a' axis in Fig. 2(b). In order to establish the minimum energy for the complex reorientation, a radial path has been considered, with the H and Zn atoms located along the a' axis. This procedure has found a radial minimum 0.24 eV higher in energy than the stable BC configuration. In order to estimate the energy barrier, that energy difference (0.24 eV) must be reduced by the zero-point-energy contribution, which corresponds to the vibrational mode driving the H motion from BC-to-BC site, i.e., the bending mode (540 cm^{-1}, see Table II).[39] This leads to an energy barrier of 0.21 eV, a value almost one order of magnitude greater than the experimental one (0.037 eV).[14] In the *minimum barrier configuration* the Zn-H and the As-H distances are equal to 1.67 Å and 1.87 Å, respectively, i.e., 2.4% and 25% greater than the values given by the covalent radii. This result as well as the plot of the total (valence) charge density for the minimum barrier configuration, see Fig. 6(b), indicate a weak bond of H with Zn and a slight interaction of H with its As nearest neighbors. The above results show that the energy barrier estimated for the reorientation of the Zn_{Ga}-H_{BC}-As complex is comparable with that experimentally found[7] for the reorientation of the Be_{Ga}-H_{BC}-As complex. This seems quite reasonable because in both complexes the H local bonding is characterized by the formation of a strong H-As bond slightly perturbed by the acceptor.[3,19]

Similar calculations have been performed in the case of the Si_{As}-H_{BC}-Ga complex. The investigated circular path for the H motion is indicated in Fig. 2(a). Once more, the total

energy increases up to a H position on the [001] axis passing through the location of the Si atom in the unrelaxed lattice; see the *a* axis in Fig. 2(a). A hydrogen radial path along this axis has then been investigated. The minimum total energy along this path is 0.22 eV higher than that of the stable complex configuration. That value is reduced to 0.17 eV by the zero-point-energy contribution (the bending mode energy is equal to 880 cm^{-1}; see Table II), thus leading to an estimate of the barrier opposing H migration in GaAs:Si in reasonable agreement with the experimental value (0.26 eV).[7] It should be noticed that, in the case of Si:B, experiments performed at about 60 K have found[10] that the energy barrier for the H motion is equal to 0.176 eV, i.e., 0.04 eV lower than that measured[9] at about 130 K (0.22 eV). If a similar correction could be applied in the case of GaAs:Si, it would improve greatly the agreement between the present estimate of the energy barrier and the experimental value. In the energy barrier configuration, the Si-H and the Ga-H distances, 1.57 Å and 2.49 Å, respectively, are 5.4% and 28% greater than the values given by the covalent radii. These atomic distances and a plot of the total (valence) charge density, see Fig. 6(a), indicate that there is a weak bonding interaction between Si and H and a slight interaction of H with its Ga nearest neighbors. The H local bonding is, therefore, quite similar to that characterizing the minimum barrier configuration in the case of the Zn acceptor. The above results show that the Zn_{Ga}-H_{BC}-As and the Si_{As}-H_{BC}-Ga complexes have a similar reorientation kinetics, which is not surprising in view of the similarities between the H local bondings in the two complexes. The same results suggest, therefore, that the reorientation of the Zn_{Ga}-H_{BC}-As complex proceeds as in the case of the Be_{Ga}-H_{BC}-As and Si_{As}-H_{BC}-Ga complexes, at least in the temperature range from 70 K to 120 K. Namely, the reorientation should be characterized by a thermally assisted process, which implies the jump of a single barrier. As a further consequence, in the above temperature range, the relaxation rates of the Zn_{Ga}-H_{BC}-As complex should be close to those given in Fig. 3 for the Be_{Ga}-H and Si_{As}-H complexes.

In conclusion, although the present results do not exclude the possibility that a deviation from an Arrhenius behavior could be observed at low temperatures, they cannot account for the high relaxation rates observed by AR measurements in the case of the Zn acceptor.[14]

A possible role of tunneling in the reorientation process has then been considered and two different models have been investigated. The first model has been already successfully introduced to account for the reorientation of nitrogen in diamond.[21] In this model, the H motion occurs in a static potential described by symmetric wells and H tunneling occurs between excited vibrational states in the potential wells, see Fig. 7. The tunneling frequency has been then estimated in the one-dimensional quasiclassical (WKB) approximation.[40] As in the case of nitrogen, two parabolic shapes of the potential barrier, labeled *pa* and *pb*, have been considered; see Fig. 7. The mode frequency of H in the potential well, ν_0, the barrier height $V(0)$, and the barrier width L are related by
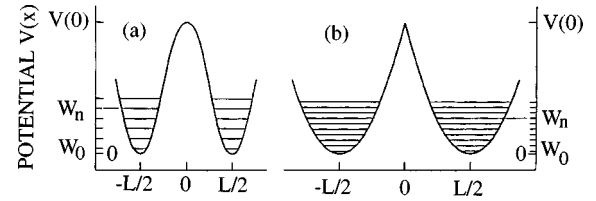
$$\pi^2 m \nu_0^2 L^2 = 4 V(0),$$

FIG. 7. Parabolic potential barriers considered in a tunneling model, which involves excited vibrational states in two symmetric wells: (a) parabolic potential, referred as *pa* in the text, and (b) parabolic potential, referred as *pb* in the text. W_0 and W_n indicate the energies of the ground and excited vibrational states, respectively. $V(0)$ indicates the energy of the barrier between the two wells and L is the barrier width. The figure is taken from Ref. 21, with permission.

for the barrier *pa*, and by

$$\pi^2 m \nu_0^2 L^2 = 2 V(0),$$

for the barrier *pb*, where m is the atomic mass.

In the case of the barrier *pa*, the former relationship is satisfied when ν_0, L, and $V(0)$ are taken equal, respectively, to the values of the H bending frequency, of the distance between the initial and final BC sites of the moving H, and of the energy barrier for the complex reorientation found by the present *ab initio* calculations. These values have been slightly changed, instead, in order to satisfy the relationship corresponding to the *pb* barrier. The reorientation frequencies at different temperatures have been estimated as in Ref. 21. In the case of deuterium, this tunneling model gives a reorientation frequency of about 10^5 s^{-1} at 20 K, which agrees reasonably with the AR experimental result, see Fig. 3. This agreement, however, might be accidental. In fact, the estimated reorientation frequency is almost constant up to 150 K, at variance with the experimental findings. Moreover, quite similar results have been obtained in the case of the Si_{As}-H complex, where much lower values of the relaxation frequency have been experimentally determined. Finally, it has to be mentioned that the experiments are performed at constant pressure, while present estimates are made at constant volume. Although these different constraints may not affect the apparent activation energy value, they could likely affect the prefactor of the relaxation frequency.

Some features of a different model of tunneling, the Flynn-Stoneham thermally assisted tunneling model, have been also analyzed. In this model, the lattice distortion caused by a light interstitial — which is relevant in the case of H_{BC} — inhibits simple tunneling. However, thermal fluctuations may give rise to a coincidence geometry in which tunneling from site to site can occur. A schematic view of the model is given in Fig. 8(a), where the effect of the lattice distortion on the shape of the potential is represented by two asymmetric wells (left and right side of the figure), while the effect of the coincidence geometry is represented by two symmetric wells (center of the figure). The jump rate depends on three parameters: (i) the thermal energy to access the coincidence geometry E_c, (ii) a tunneling matrix element, and (iii) the Debye temperature. Only a very simple test has been performed here, namely, an estimate of E_c. In the case of the Zn_{Ga}-H_{BC}-As complex, a ''natural'' choice for the coincidence geometry is represented by the geometry
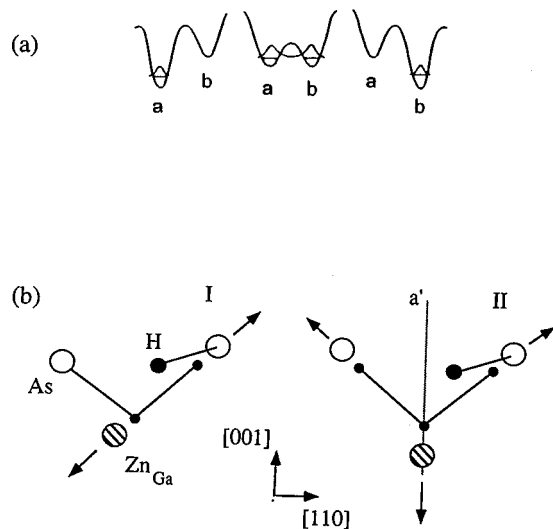
FIG. 8. (a) Scheme of potentials wells entering the Flynn-Stoneham tunneling model, see the text. (b) Equilibrium configuration for the Zn_{Ga}-H_{BC}-As complex (I); configuration proposed for the coincidence geometry discussed in the text (II).

schematized in configuration II of Fig. 8(b). This geometry is symmetric with respect to the a' axis shown in Fig. 2(b) but for the position of the H atom. In the figure, configuration I shows the Zn_{Ga}-H complex in the (110) plane and the arrows indicate the lattice distortion due to the complex formation, which is related to the asymmetric wells of Fig. 8(a). In configuration II, the Zn atom is located on the a' axis at the same distance from the two As neighbors, which are involved in the H-complex configurations at the start and at the end of the H motion. In this symmetric configuration, the potential created by the crystal surrounding the H atom may be represented by two symmetric wells separated by a potential barrier, see Fig. 8(a), which allows tunneling between two BC sites as required by the Flynn-Stoneham model. Different symmetric geometries have been considered and partially relaxed in order to minimize their total energy. The thermal energy E_c has then been estimated as the difference between the total energy of the symmetric configuration and that of the stable configuration. These calculations have

given a thermal energy E_c to access the coincidence geometry of about 0.37 eV (if one takes into account the zero-point-energy contribution), a value comparable with that of the energy barrier E_a found for the complex reorientation in the absence of tunneling (0.21 eV) but very high with respect to that obtained experimentally for the coincidence energy, 0.034 eV, from a fit of AR results within the Flynn-Stoneham model.[14] A similar estimate of the thermal energy E_c for the Si_{As}-H_{BC}-Ga complex has given a value of about 0.25 eV, once more comparable with that of the Zn_{Ga}-H_{BC}-As complex.

IV. CONCLUSIONS

The structure, the electronic properties, and the reorientation kinetics of the Si_{As}-H-Ga complex have been compared with those of the Zn_{Ga}-H-As complex. In the former case, the geometry found for the stable configuration, the structural and vibrational parameters, and the energy barrier for the complex reorientation agree well with the experimental findings. In the case of the Zn_{Ga}-H-As complex, a good agreement between theoretical and experimental results has also been found but for the high relaxation rates of the H complex measured at low temperature by AR investigations. As expected, the Zn_{Ga}-H-As complex has static and dynamic properties similar to those of the Be_{Ga}-H-As complex. The properties of the Zn_{Ga}-H-As complex are also similar to those of Si_{As}-H-Ga. Thus, the present results account for the likeness of the experimental results achieved in the cases of Ga-site acceptors (i.e., Be and Zn) and As-site acceptors (i.e., Si). On the other hand, neither the value estimated for the energy barrier opposing the reorientation of the Zn_{Ga}-H-As complex, nor the analysis of two different tunneling models have allowed to account for the high relaxation rates measured in deuterated GaAs:Zn. Furthermore, those relaxation rates appear to be quite anomalous if compared with those characterizing other H-acceptor complexes. In view of the present results, it is suggested that the relaxation rates measured in the AR experiments do not correspond to the reorientation of an isolated H-Zn complex, but, most likely, to peculiar reorientation processes involving H (D), Zn, and further defects or impurities.

*Author to whom correspondence should be addressed.

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