PHYSICAL REVIEW B, VOLUME 64, 235211

Self-interstitial–hydrogen complexes in Si

M. Gharaibeh and S. K. Estreicher
Department of Physics, Texas Tech University, Lubbock, Texas 79409-1051

P. A. Fedders
Department of Physics, Washington University, St. Louis, Missouri 63130-1105

Pablo Ordejón
Institut de Ciència de Materials de Barcelona, CSIC, Campus de la U.A.B., E-08193 Bellaterra, Barcelona, Spain

(Received 4 April 2000; revised manuscript received 2 May 2001; published 28 November 2001)

Native defects in Si are readily created during a variety of processes. They diffuse rapidly and interact with themselves, with each other, and with many impurities, in particular hydrogen. Vacancy-hydrogen complexes are better understood than self-interstitial–hydrogen ones, except for (one of) the $\{I,H_2\}$ complexes, which has been detected by infrared absorption spectroscopy and predicted theoretically. In this paper, the interactions between one neutral self-interstitial (I) and up to four hydrogen impurities are studied systematically using first-principles molecular-dynamics simulations with basis sets consisting of linear combinations of atomic orbitals. Except for $n=1$, each of the $\{I,H_n\}$ complexes has at least one metastable configuration. One family of structures has two H's bound to the same Si atom. Another family of structures has a single H bound to each Si atom, forming a "zig-zag" chain of Si-H bonds. The former complexes are more localized, with H tying up bonds at the defect itself. The latter complexes are more extended, and illustrate how H relieves the lattice strain associated with a defect. The experimentally observed $\{I,H_2\}$ complex is the most stable of the series. The configurations, stabilities, electrical activity, and spin densities are discussed. We find that total energy differences and electronic structures are sensitive to the $\vec{k}$-point sampling, even when using 128 host-atoms cells. For the type of defects discussed here, more than four $\vec{k}$ points may be needed to achieve convergence in that respect.

DOI: 10.1103/PhysRevB.64.235211 PACS number(s): 61.72.−y, 66.30.Lw, 72.10.Fk

I. INTRODUCTION

Hydrogen is a common impurity in silicon and other semiconductors. It diffuses rapidly and interacts with a wide range of impurities and native defects. These interactions often involve some degree of covalent bonding between H and Si atoms. The most common consequence is a change in the energy spectrum associated with the defect. Energy levels may shift within the gap, from the gap to a band (passivation), or from a band to the gap (activation).[1,2] The thermal stability of most complexes containing H is of the order of a few hundred °C. The most stable ones usually involve H and intrinsic defects, in particular vacancy type, because nearly ideal Si-H bonds can form. The strongest bonds occur when H binds to a perfect dangling bond, that is to a Si atom which ends up nearly sp^3 hybridized. The stretch vibrational modes of such Si-H bonds are in the 2000–2222 cm^{-1} range. Weaker Si–H bonds, with modes as low as 1800 cm^{-1} or so, correspond to Si-H bonds where Si has a different hybridization, such as H at an antibonding site (where Si is $\sim sp^2$ hybridized) or H bound to a Si atom which is off the trigonal axis, neither sp^2 nor sp^3 hybridized, as when self-interstitials (I's) are present. In the latter case, the $3d$ orbitals of Si have a nonzero population, allowing a variety of weaker Si-H bonding structures. Note that in hydrogenated amorphous Si, Si-H stretching modes around 2200 cm^{-1} are associated with H bound to a Si atom with three other Si nearest neighbors, and the lower 2000 cm^{-1} modes with two H's bound to the same Si atom with two other Si nearest neighbors.[3]

The simplest situations to study theoretically involve the strongest Si-H bonds, because the minima of the potential surface are deep and well defined, and few or no metastable configurations exist. This is generally the case for vacancy–hydrogen defects. Several complexes of the type $\{V_n,H_m\}$ have been identified theoretically[4–8] and experimentally.[9–12] It is now established that the deep levels[13] of the vacancy (V) can be fully passivated by four H atoms trapped in it, with all four Si-H bonds pointing toward the center of the vacancy (see, e.g., Ref. 7).

The four $\{V,H_n\}$ complexes have been identified by Fourier transform infrared (FTIR) absorption spectroscopy.[9,10] However, the stretch mode at 2222 cm^{-1} with T_d symmetry has been assigned to both the $\{V,H_4\}$ complex[9,10] and to the interstitial silane (SiH_4) molecule.[14,15] The empirical valence force-field calculations of Guoren *et al.*[16] favored $\{V,H_4\}$ over interstitial SiH_4. Semiempirical Hartree-Fock calculations by Frolov and Mukashev[17] of force constants for the two possible models found that the Si-H force constant of SiH_4 in silicon is substantially reduced relative to that of free SiH_4, suggesting that the high frequency observed should be associated with $\{V,H_4\}$ rather than interstitial silane. Recent first-principles calculations[18] of vibrational modes confirmed that the stretch mode of interstitial SiH_4 is close to 1800 cm^{-1}, far too low to be associated with the observed mode.

Much less is known about other $\{I,H_n\}$ complexes. Only one kind of $\{I,H_2\}$ complex has been firmly identified[19] by FTIR and *ab initio* theory. The defect has C_2 symmetry and the high-frequency local vibrational modes of the this complex are at 1987 and 1989 cm^{-1}.

The issue of hydrogen interactions with implantation or radiation damage is almost 25 years old. Stein[20] obtained the first IR spectra in H (and D) implanted silicon, and suggested that V's and I's form complexes with H. Numerous other authors later studied H-defect centers and sometimes proposed models. For example, Gerasimenko *et al.*[21] found new IR bands and studied their annealing behavior. Shi *et al.*[14] proposed that the 2222 cm^{-1} line with T_d symmetry was caused by an interstitial silane (SiH_4) molecule, and proposed the split-$\langle 100\rangle$ $\{I,\mathrm{H}_2\}$ defect for the 1946 cm^{-1} line. Suezawa[22] also proposed models for various lines in the IR spectra, and Fatima *et al.*[23] performed electrical measurements on H-defect centers. New ways to associate IR lines to different families of complexes, and new (larger) types of complexes are being examined.[24] The recent experimental work was reviewed by Mukashev *et al.*[25] It is only recently that some of the key H-defect complexes have been identified with a high degree of certainty[9–11,19] by a combination of FTIR (including uniaxial stress studies), electron paramagnetic resonance, and *ab initio* theory.

The first theoretical studies (extended Hückel in clusters) and intuition-based models of H-self-interstitial complexes emerged from Corbett's group in the 1970's (Ref. 26) and have been summarized by Shi *et al.*[27] Of note is the description of an $\{I,\mathrm{H}_2\}$ complex essentially identical to the one that would be observed[19] almost 20 years later. Deák *et al.*[28] performed semiempirical Hartree-Fock calculations in periodic clusters and found that no $\{I,\mathrm{H}_n\}$ defects are energetically favorable over the isolated I and H, except for $\{I,\mathrm{H}_2\}$. They report a metastable configuration of this defect, which has I at a puckered bond-centered site with both H's bound to it. The same metastable configuration was recently observed in *ab initio* tight-binding high-temperature molecular-dynamics simulations[29] of the reaction $I+\mathrm{H}_2\rightarrow\{I,\mathrm{H}_2\}$.

Van de Walle and Neugebauer[30] performed first-principles calculations for the $\{I,\mathrm{H}\}$ and one of the $\{I,\mathrm{H}_2\}$ complexes using density-functional theory with a plane-wave (18 Ryd cutoff) basis set, in a periodic supercell of 32 Si atoms (excluding the defect). They find that neutral I has a split-$\langle 110\rangle$ configuration. The coordinates they published show that the center of the split is off the substitutional site in the $\langle 001\rangle$ direction by 0.67 Å. The $\{I,\mathrm{H}\}$ complex is a distortion of this configuration, with H bound to I. The binding energy relative to I and isolated bond-centered hydrogen (H_{bc}) is 1.34 eV. They predict that this defect has a $(+/0)$ level 0.4 eV above the valence band (this level is occupied by one electron when the defect is neutral) and a $(0/-)$ level 0.1 eV higher. As for $\{I,\mathrm{H}_2\}$, they predict a structure rather similar to the one observed.[19] The binding energy is calculated to be about the same as for $\{I,\mathrm{H}_1\}$. They predict that $\{I,\mathrm{H}_2\}$ has no level in the gap, and should not be a trap for further H impurities.

In a recent paper,[31] Needs discussed the properties of the neutral isolated I in a $128+1$ cell using plane-wave basis sets. The most stable structure is the split-$\langle 110\rangle$ configuration and the center of the split is about 0.7 Å off the substitutional site in the (001) direction. Needs finds no deep (localized) levels associated with I and that the defect has a very low activation energy for diffusion from split-$\langle 110\rangle$ to hexagonal (0.15–0.20 eV) and among hexagonal sites (0.03–0.18 eV). A quantum Monte Carlo study[32] finds the H site to have the lowest energy by 0.14 eV in a 54 atoms cell using geometries optimized using DF within the local density approximation. However, since the isolated I has yet to be observed in Si, there is no experimental information to which theory can be compared.

In this paper, we present the results of systematic theoretical studies of the $\{I,\mathrm{H}_n\}$ family of complexes with $n=1,\ldots,4$, including the interstitial silane and silyl molecules using *ab initio* dynamic rather than static methods. By performing simulated quenching, we find a dozen local minima of the potential energy, calculate their relative stabilities, discuss the electrical activity and other properties (such as spin densities) of the more stable complexes.

II. THEORETICAL APPROACH

The preliminary results[33] were obtained from molecular-dynamics (MD) simulations in periodic supercells of 64 Si atoms (excluding the defect) and four special $\vec{k}$ points for the Brillouin zone sampling as well as a few calculations in a 216 Si atoms cell with only the Γ point. In that work, the spin-averaged, non-self-consistent Harris energy functional[34] and a minimal single-zeta (SZ) basis set of one s and three p pseudoatomic orbitals[35] per Si atom were used. A few calculations including approximate self-consistency[36] were also performed. The potential energy surface for a self-interstitial with one to four H's was explored by performing rapid quenches starting from symmetrically inequivalent initial configurations. The method is very useful to explore complicated potential energy surfaces because the small basis sets and non-self-consistent nature of the calculations substantially reduces the required computer time.

In this work, we report fully self-consistent *ab initio* calculations of the structure and energetics of self-interstitial–hydrogen complexes in Si. These density-functional (DF) calculations are done within the local spin-density approximation. The exchange-correlation potential is that of Ceperley-Adler[37] as parametrized by Perdew and Zunger.[38] Norm-conserving pseudopotentials in the Kleinman-Bylander form[39] are used to remove the core electrons from the calculations. The valence electrons are described using linear combinations of numerical atomic orbitals (LCAO) basis sets of the Sankey type,[35] but generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states.[40] In this work, a double-zeta plus polarization (DZP) basis set is used (that is two sets of s and p plus one set of d orbitals on each Si atom, and two s and one set of p orbitals on each H atom). The charge density is projected on a real space grid with equivalent cutoffs of 50 to 100 Ry to calculate the exchange-correlation and Hartree potentials. The calculations are performed using the SIESTA code.[40,41]

Note that the use of atomiclike basis sets makes it computationally difficult to test for basis-set convergence in the same way plane-wave basis sets can be tested. A sufficiently large number of plane-waves can mimic *s*, *p*, *d*, *f* and higher orbitals, and one can increase the cutoff energy to test for convergence. A comparable test of a local basis set would involve adding (i) multiple-zeta functions for each valence orbital (e.g., many sets of $3sp$ orbitals in the case of Si) and (ii) many sets of polarization function (e.g., multiple-zeta $3d$'s, $4d$'s, $4f$'s, etc., on Si). Since the calculations scale roughly as N^3 where N is the total number of orbitals, the computational effort associated with such tests becomes totally impractical. However, decades of experience with atomic basis sets have been accumulated in Hartree-Fock (HF) and post-HF calculations as well as DF calculations in clusters, and it is very well established[42] that DZ basis sets improve substantially on SZ ones, but triple or more zetas do not. Similarly, adding one set of polarization function to a DZ basis set does most of the trick, and adding multiple sets of polarization functions results in marginal corrections.[43] This is particularly true for a semiconductor such as Si. The Si $3d$ orbitals play a substantial role when dealing with large distortions (such as for the reconstruction around a vacancy), in which the Si atoms are no longer sp^3 hybridized. However, we are aware of no defect in Si for which the $4f$ orbitals of Si would contribute at all. Note that a system as complex as l-Si is very well described by SIESTA, even with a minimal basis set,[44] although the basis set is obviously not converged.

On the other hand, given a reasonably large basis, varying the cell size as well as the $\vec{k}$-point sampling plays a much more important role than improving the basis set beyond DZP. In the present and other work,[45,46] we have extensively tested these issues. For cells as large as 128 host atoms, we do find that using only the Γ point ($k=0$) is not enough for accurate static ($T=0$ K) results. In many situations, using four special $\vec{k}$ points or a $2\times2\times2$ Monkhorst-Pack sampling[47] is necessary and sufficient (the maximum force changes no more by using a $3\times3\times3$ mesh, for example). However, the present work includes an example (the self-interstitial) where the presence of gap levels does depend on the $\vec{k}$-point sampling beyond a $2\times2\times2$ mesh.

In this paper, MD simulations are performed using DF quantum-mechanical forces. The ions are treated as classical particles and the electrons remain at 0 K on the Born-Oppenheimer surface. Simulated quenching with a time step of 2.0 fs (0.2 fs with H in the cell) provides the equilibrium configurations and potential energy differences. The host crystal is represented by a periodic supercell of 64 or 128 host atoms (excluding the defect) with $\vec{k}$-point sampling varying from the Γ point only to a $3\times3\times3$ mesh. All the configurations obtained earlier[33] were quenched again, and new ones explored, with and without spin polarization.

III. RESULTS

In agreement with all other DF calculations,[30,31,48–52] we find that the isolated neutral self-interstitial has the split-$\langle 110\rangle$ configuration. The center of the split is shifted by 0.80 Å in the $\langle 001\rangle$ direction. The structure is shown in Fig. 1 in the 64 host atoms cell. The calculated formation energy of the self-interstitial is 3.33 eV in the 128 host atoms cell, a DZP basis set, and a $2\times2\times2$ $\vec{k}$-point sampling, in complete agreement with other authors (see, e.g., Ref. 31).

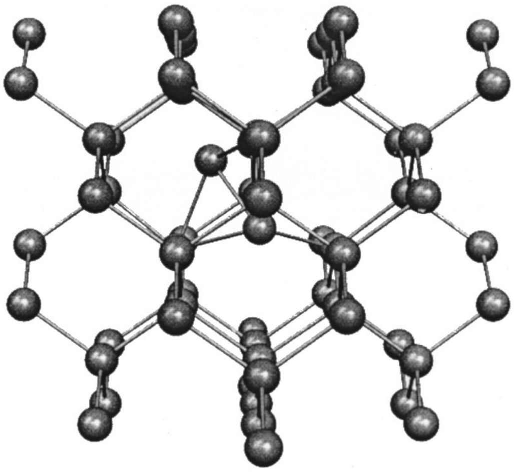

FIG. 1. The isolated neutral self-interstitial has a split-$\langle 110\rangle$ configuration. the center of the split is shifted by 0.76 Å in the $\langle 001\rangle$ direction.

The hexagonal interstitial site is also a local minimum of the potential energy for the neutral self-interstitial, 0.35 eV above the split-$\langle 110\rangle$ ground state. However, this site is not stable upon heat treatment: a 1000 K constant-temperature MD simulation for 1000 time steps followed by quenching forces the self-interstitial into the split-$\langle 110\rangle$ configuration.

Our calculations show that at least four H's can trap at a neutral self-interstitial. The configurations range from a series of Si-H bonds on adjacent Si atoms to several H's bound to a single Si atom. Our notation for these structures is (n)-(m)-$\cdots$, meaning n H's bound to one Si atom, m H's bound to the adjacent Si atom, etc.

The only possibility for $\{I,H_1\}$ is (1), but $\{I,H_2\}$ can be (2) or (1)-(1). The three possibilities for $\{I,H_3\}$ are (3) (the interstitial silyl molecule SiH_3), (2)-(1), and (1)-(1)-(1). Finally, the possibilities for $\{I,H_4\}$ are (4) (the interstitial silane molecule SiH_4), (3)-(1), (2)-(2), (2)-(1)-(1), (1)-(2)-(1), and (1)-(1)-(1)-(1).

The stability of each complex was calculated as the largest possible gain in energy ΔE_n obtained by adding isolated H_{bc} to the most stable of the $\{I,H_{n-1}\}$ complexes:

$$\{I,H_{n-1}\}+H_{bc}\rightarrow\{I,H_n\}+\Delta E_n\,.$$

Thus, if a thermal anneal breaks up a given $\{I,H_n\}$ complex into the most stable $\{I,H_{n-1}\}$ complex and H_{bc}, then ΔE_n is the binding energy.

Table I gives the ΔE_n's calculated in the 128 host-atoms cell with a DZP basis set and spin polarization, with either only the Γ point or a $2\times2\times2$ mesh. Note that which configuration of $\{I,H_n\}$ has the lowest energy is independent of the number of $\vec{k}$ points, but the binding energies vary significantly. The geometries of the various structures do not depend very much at all on the $\vec{k}$-point sampling, but the energies do. Two configurations of $\{I,H_2\}$, (2) and (1)-(1), are

TABLE I. ΔE_n(eV) is the energy gained by forming $\{I,\mathrm{H}_n\}$ starting with the most stable $\{I,\mathrm{H}_{n-1}\}$ and $\mathrm{H}_{\mathbf{bc}}$. The energies were obtained from conjugate gradient calculations in the 128-host atoms cell, double-zeta polarized basis sets, spin polarization, with either only $k=0$ or a $2\times2\times2$ Monkhorst-Pack sampling. The most stable configuration of each $\{I,\mathrm{H}_n\}$ complex is in bold. Three structures are not listed: they correspond to complexes which should not form: (1)-(1)-(1)-(1) has $\Delta E_n \sim 0$ while (3) and (4) have $\Delta E_n < 0$.

complex	configuration	Γ ΔE_n (eV)	$2\times2\times2$ ΔE_n (eV)
$\{I,\mathrm{H}_1\}$	(**1**)	**1.36**	**1.65**
$\{I,\mathrm{H}_2\}$	(**1**)-(**1**)	**1.75**	**1.85**
	(2)	1.65	1.80
$\{I,\mathrm{H}_3\}$	(**1**)-(**1**)-(**1**)	**1.39**	**1.26**
	(2)-(1)	0.76	0.62
$\{I,\mathrm{H}_4\}$	(**3**)-(**1**)	**0.99**	**1.35**
	(1)-(2)-(1)	0.94	1.18
	(2)-(2)	0.70	1.05
	(2)-(1)-(1)	0.87	0.87

very close in energy. The former has yet to be detected experimentally. The structures not listed in the table [they are (1)-(1)-(1)-(1), interstitial silyl (3), and interstitial silane (4)], have $\Delta E_n \leqslant 0$ and should not form. Note that constant-temperature MD simulations have shown[29] that the reaction $I+\mathrm{H}_2 \rightarrow (1)-(1)$ occurs with a substantial gain in energy. Thus, we do not expect interstitial H_2 molecules to form under the conditions described in this work. Further, the formation of the H_2^* complex appears to require[53] the presence of vacancies as well as self-interstitials.

Figure 2 shows how the largest ΔE_n varies with n. Following the maximum for $\{I,\mathrm{H}_2\}$ in the (1)-(1) configuration, the energy gain drops with n. Figure 3 shows the stable and selected metastable configurations, drawn within the familiar primitive cube.

The $\{I,\mathrm{H}_2\}$ complexes are the most stable of the entire series. Of those, the (1)-(1) structure energetically preferred. It is the one that has been identified experimentally and predicted by a number of authors (see the Introduction). The metastable structure (2) was first predicted by Deák *et al.*[28] then observed to form in MD simulations[29] of the reaction $I+\mathrm{H}_2 \rightarrow \{I,\mathrm{H}_2\}$.

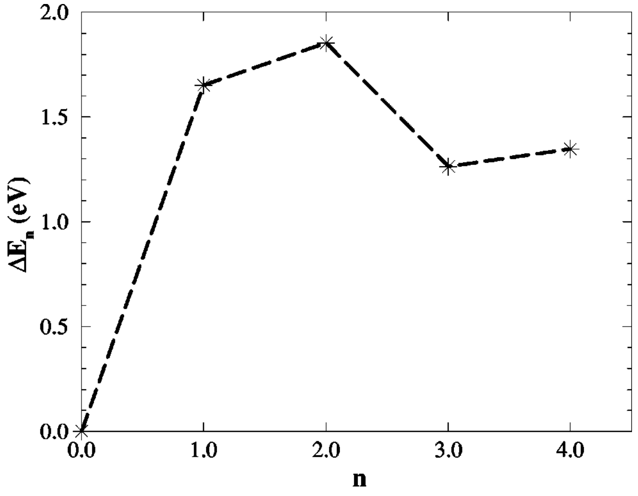

FIG. 2. Energy gained (in eV) by forming the most stable $\{I,\mathrm{H}_n\}$ complex from the most stable $\{I,\mathrm{H}_{n-1}\}$ and isolated $\mathrm{H}_{\mathbf{bc}}$.

The next-most stable complexes are $\{I,\mathrm{H}_1\}$, then $\{I,\mathrm{H}_3\}$ in the (1)-(1)-(1) configuration. In the case of $\{I,\mathrm{H}_4\}$, (3)-(1) is closely followed by (1)-(2)-(1). Experimentally,[19] the (1)-(1) complex anneals out at 225 °C. Since this is the most stable of all $\{I,\mathrm{H}_n\}$'s, we expect that only the $\{I,\mathrm{H}_1\}$ and $\{I,\mathrm{H}_2\}$ complexes are stable at or above room temperature. The vacancy-H complexes have calculated binding energies of the order of 3 eV or more,[54] and are stable up to much higher temperatures. Further, under conditions of high H implantation, there are too many defects at which H could trap with much larger binding energies to expect the $\{I,\mathrm{H}_3\}$ and $\{I,\mathrm{H}_4\}$ to form in significant amounts. Thus, we expect that only $\{I,\mathrm{H}_1\}$ and the two $\{I,\mathrm{H}_2\}$ give rise to FTIR lines. Finally, our energetics confirm the conclusions of *ab initio* calculations of vibrational modes[18] that the 2222 cm^{-1} is not due to interstitial silane.

The atomic spin density for $\{I,\mathrm{H}_1\}$ show that 40% of the odd electron resides on two Si nearest-neighbors (NN's) to the Si-H bond. These two atoms are marked with "0.2" in Fig. 4. Another 25% of the spin is spread around further 8 NN's, and the rest is delocalized in the supercell. In the case of $\{I,\mathrm{H}_3\}$ in the (1)-(1)-(1) configuration, only 20% of the spin is localized, 10% on each of the two Si atoms marked "0.1" in Fig. 4. As for the (2)-(1) complex, the odd electron is fully delocalized in the cell.

The electronic structure of these defects is an important issue as it determines their electrical behavior. A defect may induce localization of carriers (if levels are present in the gap). The passivation of defect levels is also an important issue when considering interactions between defects and impurities such as H. Our calculations allow us to address this issue in a qualitative way from the LDA spectrum.

For the split-$\langle 110 \rangle$ self-interstitial, our results show the presence of a defect band below the conduction band edge of the perfect Si crystal. We find that the position of the defect states within the gap is strongly dependent on the values of the *k* points used to compute the band energies. This indicates that these states are not very localized and that the interaction of these states in neighbor image cells is strong enough to produce a significant dispersion.

Figures 4 shows the dispersion of the energy bands in the Brillouin zone calculated in the 128 host-atoms cell with a DZP basis set and 30 $\vec{k}$ points. The figures show the band structures of (a) the perfect cell, (b) the split-$\langle 110 \rangle$ self-interstitial, and (c) the $\{I,\mathrm{H}_2\}$ complex in the (1)-(1) configuration. The band gap of the perfect cell (0.48 eV) agrees well with that obtained with plane waves by Needs[31] (0.55 eV), even though the latter was calculated using the experimental lattice constant of Si, whereas we have used the one that minimizes the energy with our LDA functional, pseudopotential and basis set. The band structure of the cell with a self-interstitial shows a defect-related band with significant dispersion, well below the conduction band minimum of the

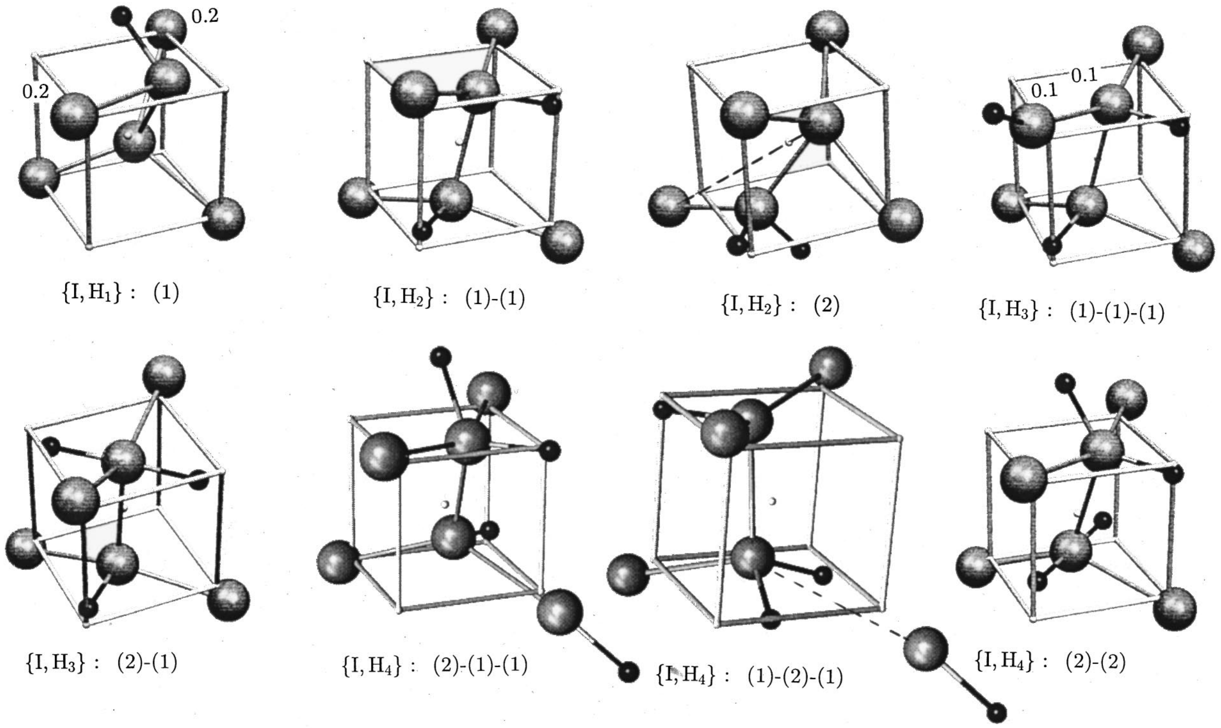

FIG. 3. Various stable $\{I,\mathrm{H}_n\}$ complexes shown in the primitive cell. The substitutional site in the center of the cube is drawn as a small circle. The H atoms are in black. In the case of the (2) structure of $\{I,\mathrm{H}_2\}$, the relevant trigonal axis is dashed. For $\{I,\mathrm{H}_1\}$ and $\{I,\mathrm{H}_3\}$, the localized fraction of the odd electron is indicated (see text). The stability of the various complexes is given in the table.

host Si crystal in much of the Brillouin zone. Such a large dispersion indicates that the defect states are not highly localized. The localization length is certainly larger than the unit cell size. Therefore, we cannot decide at this point what would be the exact location of the defect state for a single interstitial in Si, since calculations in much larger unit cells would be required. However, our results tend to indicate that this defect may induce a state no more than ~ 0.2 eV below the conduction band edge. Finally, the band structure of $\{I,\mathrm{H}_2\}$ in the (1)-(1) configuration shows very good passivation, as predicted by other authors.[30]

Several authors have examined the electrical activity of the split-$\langle 110\rangle$ self-interstitial[31,55] and concluded that there is no defect level in the gap or, at most, a very shallow one. This conclusion was drawn from the band energies obtained from a $2\times2\times2$ k-point sampling, for which the gap of the cell with the self-interstitial was 0.51 eV (only slightly smaller than the LDA 0.55 eV band gap of the host Si crystal). We do get a number very close to that of Needs when using the $2\times2\times2$ mesh: 0.52 eV. However, as seen in Fig. 4, this number drops considerably when more $\vec{k}$ points are considered. Therefore, the localization of the impurity level may be higher than expected.

In order to compare the band structures of different cells, they should be brought to a common origin of the energies because the zero of the potential is different for each cell. Part of the Coulomb potential is computed in reciprocal space using fast Fourier transforms (FFT's) and the zero of the energy is taken to be the average value of that potential, which is different in each cell. In SIESTA, in contrast with plane-wave methods, only the contribution to the Hartree potential which comes from $\delta\rho$ (the difference between the actual self-consistent charge density and the sum of the densities of all the free atoms at every point) is computed by means of an FFT.[41] Since the present situation involves little charge transfer, the misalignment of the potential energies of different cells is expected to be small. We have checked this by comparing the values of the macroscopic potential[56] in the defect-free cell to that of the cell with the self-interstitial far from the defect itself. The mismatch is below 0.01 eV, and is only slightly larger for the (1)-(1) defect. Therefore, we have neglected these effects when plotting Fig. 4.

IV. DISCUSSION

Simulated quenching of the $\{I,\mathrm{H}_n\}$ complexes with $n = 0,\ldots,4$ has been performed using self-consistent *ab initio* LCAO MD simulations based on DF theory. Our calculations used DZP basis sets with spin polarization or spin averaging in 64 and 128 host-atoms cells. The $\vec{k}$-point sampling ranged from the Γ point only to a $3\times3\times3$ Monkhorst-Pack mesh. Simulated quenching was used to find the local minima of the potential energy surface for the neutral self-interstitial and twelve configurations of $\{I,\mathrm{H}_n\}$. The binding energy of each complex was defined as the energy gained by forming a particular configuration of $\{I,\mathrm{H}_n\}$ from the most stable $\{I,\mathrm{H}_{n-1}\}$ plus isolated $\mathrm{H}_{\mathbf{bc}}$.

The most stable structure is the experimentally observed $\{I,\mathrm{H}_2\}$ defect in the (1)-(1) configuration, with $\Delta E = 1.85$ eV. Then come the (2) and (1) complexes with bind-

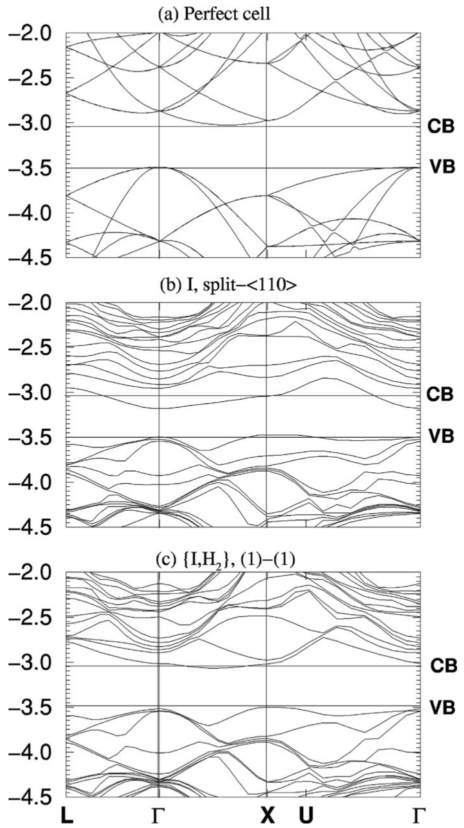

FIG. 4. Dispersion of the energy bands in the Brillouin zone calculated in the 128 host-atoms cell with a DZP basis set and 30 $\vec{k}$ points. The figures show the band structures of (a) the perfect cell, (b) the split-$\langle 110\rangle$ self-interstitial, and (c) the $\{I,\text{H}_2\}$ complex in the (1)-(1) configuration.

ing energies of 1.80 and 1.65 eV, respectively. All the other $\{I,\text{H}_n\}$ complexes have much smaller binding energies. In contrast, the trapping of one or more H's at a vacancy involves binding energies[7] of the order of 3 eV. The interstitial silyl and silane molecules have negative ΔE_n's and should not form in crystalline silicon.

Our results show that H can trap at lattice strain (provided here by the self-interstitial). Hydrogen relieves the strain by forming a zig-zag chain of adjacent Si-H bonds with, occasionally, two H's bound to the same Si atom.

$\{I,\text{H}_1\}$ has 40% of the odd electron localized (20% on each of two Si atoms) and $\{I,\text{H}_3\}$ in the (1)-(1)-(1) configuration has only 20% of the odd electron localized (10% on each of two Si atoms). The rest of the spin, and all of it in the case of the (2)-(1) structure, is delocalized over the entire cell.

It is often assumed that supercell calculations are converged with respect to $\vec{k}$-point sampling with a single $\vec{k}$ point already for the 64-atoms cell. We find that this assumption is not correct. Geometry optimizations with conjugate gradients and the Γ point only were performed down to maximum forces less than 0.03 eV/Å. If a $2\times2\times2$ mesh is added to the converged geometry, the maximum force increases to 0.10 or even 0.30 eV/Å, and further geometry optimizations with multiple $\vec{k}$ points are needed. Total energy differences are affected, as well as some features of the band structures. However, going from 4 to 30 $\vec{k}$ points does not make anywhere near as much difference as going from 1 to 4. The geometries obtained with a single $\vec{k}$ point are quite good.

Band-structure calculations in the 128 host-atoms cell show that the split-$\langle 110\rangle$ self-interstitial may induce a state more localized than previously believed.[31,55] Our calculations also predict that the $\{I,\text{H}_2\}$ complex is passivated, in agreement with earlier predictions.[30] However, we find a metastable structure for $\{I,\text{H}_2\}$ with a rather high stability, as well as numerous more weakly bound structures for $\{I,\text{H}_n\}$ with $n>2$.

We disagree with Needs[31] and recent Monte Carlo calculations/cite{qmc} (based on the same geometries) regarding the stability of the hexagonal interstitial site for the self-interstitial. We find that site to be unstable. I converts to the split-$\langle 110\rangle$ configuration after a quench following a 1000 time step run at 1000 K.

On the other hand, we do agree quantitatively, or at least qualitatively, with the results in Refs. 30,31 on much of the energetics and/or configurations of the most stable complexes. We agree about the structure of the neutral self-interstitial, in particular that its center is shifted by about 0.7–0.8 Å in the $\langle 001\rangle$ direction. We agree with Ref. 30 that $\{I,\text{H}_1\}$ and $\{I,\text{H}_2\}$ are stable structures with rather large binding energies. We find nearly identical geometries as those in Refs. 26,28,30 for the most stable complexes $\{I,\text{H}_1\}$ and $\{I,\text{H}_2\}$.

Some of the differences could arise from the size of the cell used to represent the host crystal. It is 32 Si atoms in Ref. 30 and 128 Si atoms in the present work. Some of our calculations[33] were also done in 64 and 216 Si atom cells and, in the case of the complexes studied here, only minor differences with cell size were noted. The cell must be large enough to accommodate a complex of up to 5 atoms and the strain associated with it. As noted by Allan and Joannopoulos,[57] since the Si-H bond is stronger than the Si-Si bond, the hydrogenation of amorphous Si increases the size of the average matrix element and thus increases the size of the gap. The effect is important even for H concentrations well below 10%. In the 32-Si cell, two H's may suffice to compensate for the reduction of the size of the gap induced by the strain. The calculation of local vibrational modes associated with the $\{I,\text{H}_n\}$ complexes and other defects will be published separately.[58]

ACKNOWLEDGMENTS

The work of S.K.E. was supported in part by a grant from the R.A. Welch Foundation, a contract from the National Renewable Energy Laboratory, and a research award from the Humboldt Foundation. P.O. acknowledges the support of the Fundación Ramón Areces (Spain) and the Grant No. BFM2000-1312-CO2-01 from Spain's MCyT. Many thanks to the High Performance Computing Center at Texas Tech's Institute for Environmental and Human Health for generous amounts of computer time.

[1] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992).

[2] S.K. Estreicher, Mater. Sci. Eng., R. **14**, 319 (1995).

[3] G. Lucovsky and W. B. Pollard, in *Hydrogenated Amorphous Silicon*, Vol. 56 of Topics in Applied Physics (Springer, Berlin, 1984), p. 301.

[4] V.A. Singh, C. Weigel, J.W. Corbett, and L.M. Roth, Phys. Status Solidi B **81**, 637 (1977).

[5] P. Deák, L.C. Snyder, M. Heinrich, C.R. Ortiz, and J.W. Corbett, Physica B **170**, 253 (1991).

[6] H. Xu, Phys. Rev. B **46**, 1403 (1992).

[7] Y.K. Park, S.K. Estreicher, C.W. Myles, and P.A. Fedders, Phys. Rev. B **52**, 1718 (1995); M.A. Roberson and S.K. Estreicher, *ibid.* **49**, 17 040 (1994).

[8] C.G. Van de Walle and R.A. Street, Phys. Rev. B **49**, 14 766 (1994).

[9] B. Bech Nielsen, L. Hoffmann, M. Budde, R. Jones, J. Goss, and S. Öberg, Mater. Sci. Forum **196-201**, 933 (1995).

[10] B. Bech Nielsen, L. Hoffmann, and M. Budde, Mater. Sci. Eng., B **36**, 259 (1996).

[11] P. Stallinga, P. Johannesen, S. Herstom, K. Bonde Nielsen, B. Bech Nielsen, and J.R. Byberg, Phys. Rev. B **58**, 3842 (1998).

[12] M. Bruni, D. Bisero, R. Tonini, G. Ottaviani, G. Queirolo, and R. Bottini, Phys. Rev. B **49**, 5291 (1994).

[13] G. D. Watkins, in *Defects and Diffusion in Silicon Processing*, edited by T. Diaz de la Rubia *et al.*, MRS Symp. Proc. No. 469, (Materials Research Society, Pittsburgh, 1997), p. 139.

[14] T.S. Shi, L.M. Xie, G.R. Bai, and M.W. Qi, Phys. Status Solidi B **131**, 511 (1985).

[15] M. Suezawa, Jpn. J. Appl. Phys. **37**, L259 (1998); This line was reassigned to the $\{V,\mathrm{H}_4\}$ complex in M. Suezawa, *ibid.* **38**, L608 (1999).

[16] B. Guoren, Z. Jiankun, C. Jianmin, S. Tianshen, Q. Mingwei, and X. Leiming, Sci. Sin., Ser. A **31**, 499 (1988).

[17] V.V. Frolov and B.N. Mukashev, Phys. Status Solidi B **148**, K105 (1988).

[18] B. Hourahine, R. Jones, S. Öberg, and P.R. Briddon, Phys. Rev. B **59**, 15 729 (1995).

[19] M. Budde, B. Bech Nielsen, P. Leary, J. Goss, R. Jones, P.R. Briddon, S. Öberg, and S.J. Breuer, Phys. Rev. B **57**, 4397 (1998).

[20] H.J. Stein, J. Electron. Mater. **4**, 159 (1975); Phys. Rev. Lett. **43**, 1030 (1979).

[21] N.N. Gerasimenko, M. Rollé, L.-J. Cheng, Y.H. Lee, J.C. Corelli, and J.W. Corbett, Phys. Status Solidi B **90**, 689 (1978).

[22] M. Suezawa, Mater. Sci. Forum **258-263**, 229 (1997); Jpn. J. Appl. Phys. **37**, L259 (1998); J. Appl. Phys. **86**, 4865 (1999).

[23] S. Fatima, C. Jagadish, J. Lalita, B.G. Svensson, and A. Hállen, J. Appl. Phys. **85**, 2562 (1999).

[24] S.Zh. Tokmoldin, B.N. Mukashev, Kh.A. Abdullin, and Yu.V. Gorelkinskii, Physica B **273-274**, 204 (1999).

[25] B.N. Mukashev, Kh.A. Abdullin, Yu.V. Gorelkinskii, and S.Zh. Tokmoldin, Mater. Sci. Eng., B **58**, 171 (1999).

[26] C. Weigel and J.W. Corbett, Z. Phys. B **23**, 233 (1976); Y.H. Lee, N.N. Gerasimenko, and J.W. Corbett, Phys. Rev. B **14**, 4506 (1976); R. L. Kleinhenz, Y. H. Lee, V. A. Singh, P. M. Mooney, A. Jaworowski, L. M. Roth, J. C. Corelli, and J. W. Corbett, in *Defects and Radiation Effects in Semiconductors 1978*, edited by J. H. Albany, IOP Conf. Ser. No 46 (IOP, Bristol, 1979), p. 200.

[27] T.S. Shi, S.N. Sahu, G.S. Oehrlein, A. Hiraki, and J.W. Corbett, Phys. Status Solidi B **74**, 329 (1982).

[28] P. Deák, M. Heinrich, L.C. Snyder, and J.W. Corbett, Mater. Sci. Eng., B **4**, 57 (1989); P. Deák, L.C. Snyder, M. Heinrich, C.R. Ortiz, and J.W. Corbett, Physica B **170**, 253 (1991).

[29] S.K. Estreicher, J.L. Hastings, and P.A. Fedders, Phys. Rev. B **57**, R12 663 (1998).

[30] C.G. Van de Walle and J. Neugebauer, Phys. Rev. B **52**, R14 320 (1995).

[31] R.J. Needs, J. Phys.: Condens. Matter **11**, 10 437 (1999).

[32] J.-W. Leung, R.J. Needs, G. Rajagopal, S. Itoh, and S. Ihara, Phys. Rev. Lett. **83**, 2351 (1999).

[33] J.L. Hastings, M. Gharaibeh, S.K. Estreicher, and P.A. Fedders, Physica B **273-274**, 216 (1999).

[34] J. Harris, Phys. Rev. B **40**, 1770 (1990).

[35] O.F. Sankey and D.J. Niklevski, Phys. Rev. B **40**, 3979 (1989); O.F. Sankey, D.J. Niklevski, D.A. Drabold, and J.D. Dow, *ibid.* **41**, 12 750 (1990).

[36] A.A. Demkov, J. Ortega, O.F. Sankey, and M.P. Grumbach, Phys. Rev. B **52**, 1618 (1995).

[37] D.M. Ceperley and B.J. Adler, Phys. Rev. Lett. **45**, 566 (1980).

[38] S. Perdew and A. Zunger, Phys. Rev. B **32**, 5048 (1981).

[39] L. Kleiman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[40] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J.M. Soler, Phys. Status Solidi B **215**, 809 (1999).

[41] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).

[42] See e.g., W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab-initio Molecular-orbital Theory* (Wiley, New York, 1986).

[43] J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho, cond-mat/0104170 (unpublished).

[44] G. Fabricius, E. Artacho, D. Sánchez-Portal, P. Ordejón, D.A. Drabold, and J.M. Soler, Phys. Rev. B **60**, R16 283 (1999).

[45] S.K. Estreicher, M. Gharaibeh, P.A. Fedders, and P. Ordejón, Phys. Rev. Lett. **86**, 1247 (2001).

[46] S.K. Estreicher, K. Wells, P.A. Fedders, and P. Ordejón, J. Phys.: Condens. Matter **13**, 6271 (2001).

[47] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[48] Y. Bar-Yam and J.D. Joannopoulos, Phys. Rev. Lett. **52**, 1129 (1984).

[49] R. Car, P.J. Kelly, A. Oshiyama, and S.T. Pantelides, Phys. Rev. Lett. **54**, 360 (1985).

[50] D.J. Chadi, Phys. Rev. B **46**, 9400 (1992).

[51] P.E. Blöchl, E. Smargiassi, R. Car, D.B. Laks, W. Andreoni, and S.T. Pantelides, Phys. Rev. Lett. **70**, 2435 (1993).

[52] M. Gharaibeh, S.K. Estreicher, and P.A. Fedders, Physica B **273-274**, 532 (1999).

[53] S.K. Estreicher, J.L. Hastings, and P.A. Fedders, Phys. Rev. Lett. **82**, 815 (1999).

[54] S.K. Estreicher, J.L. Hastings, and P.A. Fedders, Mater. Sci. Eng., B **58**, 31 (1999).

[55] R. Car, P.E. Blöchl, and E. Smargiassi, Mater. Sci. Forum **83-87**, 443 (1992).

[56] A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).

[57] D. Allan and J.D. Joannopoulos, in *Hydrogenated Amorphous Silicon*, Vol. 56 of *Topics in Applied Physics* (Springer, Berlin, 1984), p. 5.

[58] J.M. Pruneda, S.K. Estreicher, J. Junquera, J. Ferrer, and P. Ordejón, cond-mat/0109306 (unpublished).