

## Theoretical study of H-P and H-B complexes in silicon

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(Received 19 September 1994)

The microscopic structures of hydrogen in donor- and acceptor-doped silicon have been studied with *ab initio* calculations based on the density-functional theory. Some results are found to have a strong dependence on the supercell size. By using a 64-atom supercell and a large plane-wave basis set (with a 22-Ry kinetic-energy cutoff), quantitative agreements with existing experimental data have been achieved for the equilibrium geometries and vibrational properties of Si-H-P and Si-H-B systems. The investigation also predicts a low vibrational frequency for the H-wagging mode in the Si-H-B complex.

### I. INTRODUCTION

Hydrogen is present throughout the manufacture process of silicon devices. It passivates donor and acceptor impurities by forming complexes in the lattice, thus affecting the electronic properties of the system. Therefore, this passivation phenomenon has been the object of a large number of investigations.<sup>1,2</sup> Experiments such as ion-channeling<sup>3</sup> and infrared-absorption<sup>4-6</sup> studies have been conducted to determine the atom positions and H vibrational spectra. Theoretically, various techniques have been applied, including semi-empirical procedures,<sup>7</sup> Hartree-Fock cluster calculations,<sup>8-10</sup> and the approach based on the density-functional theory.<sup>11-15</sup> Results from these theoretical and experimental studies compare well qualitatively for many relevant parameters. It has been agreed upon that if the impurity is boron (an acceptor), then in the equilibrium configuration H is located close to a bond-center position of the Si-B bond. For the case of a phosphorus (a donor) impurity, H is found at the Si side of the extension of a Si-P bond. In both systems, the atoms around the H would relax accordingly.

Despite much previous effort, the theoretical studies are not always satisfactory, there remain significant quantitative differences between some calculated results and the experimental data. For example, in the system of a B-H complex in Si, the evaluated distance between the equilibrium and unrelaxed positions of the B atom,  $\Delta B$ , varies from 0.55 Å (Ref. 7) to 0.42 Å,<sup>15</sup> whereas a substantially lower value of 0.28 Å has been observed in an ion-channeling experiment.<sup>3</sup> In addition, there has been a lack of first-principle approaches to the understanding of properties such as the low-frequency H-wagging vibration in the Si-H-B complex, because a high resolution is required to distinguish the slight change in total energy when the H atom is off the trigonal axis.

A powerful *ab initio* approach often used in the study of impurities in semiconductors is the density-functional method (DFM). It allows one to mimic the environment around the impurity and obtain reliable results, especially when the supercell size and the basis set are reasonably large. Unfortunately, this requires tremendous

computational resources. Therefore, supercells containing 8 or 16 atoms have been commonly adopted previously. A 32-atom supercell has been occasionally used<sup>15</sup> with the sacrifice in the size of the basis set. In this work we wish to examine how these parameters affect the results obtained using the DFM, and to pursue further improvements. By implementing a direct energy minimization technique, we are able to investigate the microscopic structures using relatively large supercells and basis sets. This is shown to be beneficial in the study of Si containing P-H and B-H complexes.

The paper is organized as follows: The detail of our DFM program is discussed in Sec. II. There we also examine the dependency of calculated electronic structures and physical properties on the kinetic-energy cutoff and the supercell size. Using a 64-atom supercell and a 22-Ry cutoff (which yields over 15 000 plane waves in the basis set), equilibrium structures for hydrogen in boron- and phosphorus-doped silicon are obtained and presented in Secs. III and IV, respectively, along with the evaluated H vibrational frequencies in these two systems. Section V is reserved for conclusions.

### II. CALCULATIONAL DETAILS

In this work we carry out *ab initio* total-energy calculations (within the plane-wave basis) which are based on the density-functional theory.<sup>16-18</sup> In the program, the Kleinman-Bylander decoupling form<sup>19</sup> of the norm-conserving pseudopotential developed by Troullier and Martins<sup>20</sup> is adopted, and for the exchange-correlation potential in the local density approximation (LDA) we employ commonly accepted results of Ceperley and Alder<sup>21</sup> as parametrized by Perdew and Zunger.<sup>22</sup> Integrations over the first Brillouin zone are replaced by summations over special  $\mathbf{k}$  points generated with the extended Monkhorst-Pack scheme by Froyen.<sup>23</sup> Throughout the calculation, the Froyen parameter  $n = 2$  is chosen, corresponding to 8  $\mathbf{k}$  points in the first Brillouin zone of a lattice with simple-cubic structure. The Kohn-Sham Hamiltonian is diagonalized by taking ad-

vantage of a recently developed direct energy minimization technique.<sup>24–26</sup> Equilibrium configurations of the systems are reached by allowing all atoms within the supercell to relax without assuming any symmetry. This is accomplished by first calculating the force on each ion using the Hellmann-Feynman formalism,<sup>27</sup> then determining new positions of the ions with the geometry optimization by direct inversion in the iterative subspace method<sup>28</sup> combined with the Broyden-Fletcher-Goldfarb-Shanno algorithm<sup>29</sup> for updating the Hessian matrix.

To investigate the properties of semiconductors containing impurities, one can construct periodically repeated supercells that are replicas of the impurity complex (e.g., P-H or B-H) and its neighboring host atoms (Si). In this way, some of the original lattice symmetry is restored and the microscopic structure of the supercell can then be determined using the DFM procedure described above. To keep the effect of artificially introduced interactions between the impurity complexes in different supercells minimal, the size of the supercell should be as large as possible. Also, in order to obtain an accurate electron density and total energy, it is necessary to adopt a reasonably large plane-wave basis set, which is determined by the kinetic-energy cutoff  $E_c$ . In this section we examine how these two parameters (the supercell size and the kinetic-energy cutoff) affect the calculated results.

To find a reasonable value for  $E_c$ , we choose to calculate the total energy of a Si-H-B complex with a fixed geometry: the bond minimum configuration used in Ref. 15. Namely, a H atom is placed near the center of a Si-B bond, and the Si and B atoms relax outward by 0.24 Å and 0.42 Å, respectively, yielding a H-Si distance of 1.64 Å. All other Si atoms in the supercell are kept fixed to their undisturbed lattice positions. Obviously not representing the optimized equilibrium geometry, however, it is sufficient for the purpose of investigating how the obtained total energy depends on  $E_c$ .

For 8-, 16-, 32-, and 64-atom supercells (representing impurity separations of  $a$ ,  $\sqrt{2}a$ ,  $\sqrt{3}a$ , and  $2a$ , respectively, with  $a$  the lattice constant), the Kohn-Sham energy functional has been minimized for various values of  $E_c$ , and the results are shown in Fig. 1. For direct comparison, in the calculated total energies for each supercell, the energy value of pure Si obtained using the same supercell size at the largest  $E_c$  has been subtracted. Figure 1 indicates that reliable results can be reached for an  $E_c$  around 20 Ry.

The supercell size also plays an important role in resulted microscopic structures and relevant properties. In Fig. 2 the band structures for the Si-H-B complex in 8- and 64-atom supercells are shown, which have been obtained using fully relaxed configurations. Comparing with the band structure for the pure Si lattice [Fig. 2(c)], it is seen that the two lowest conduction bands are lowered in the presence of B and H, thus reducing the semiconducting band gap. The study of partial densities indicates that these two bands, the lowest and second-lowest conduction bands (at the  $\Gamma$  point) are dominated by contributions from H-B and B-Si interactions, respectively.

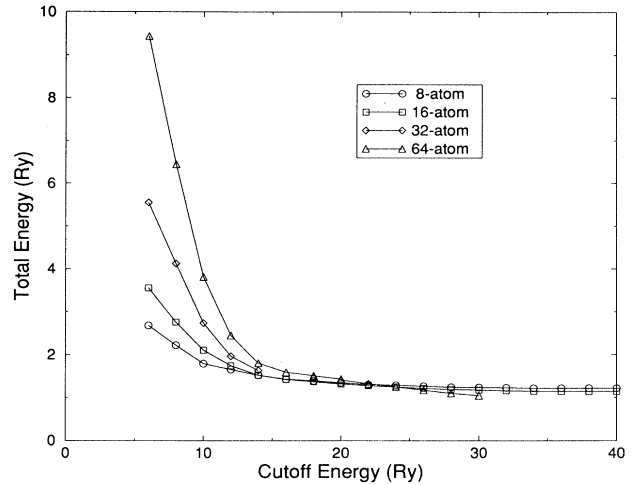


FIG. 1. The total energy for a particular configuration of the Si-H-B complex as a function of the kinetic-energy cutoff for various supercells. To make direct comparison, the results have been shifted by corresponding total energy values for the pure Si lattice.

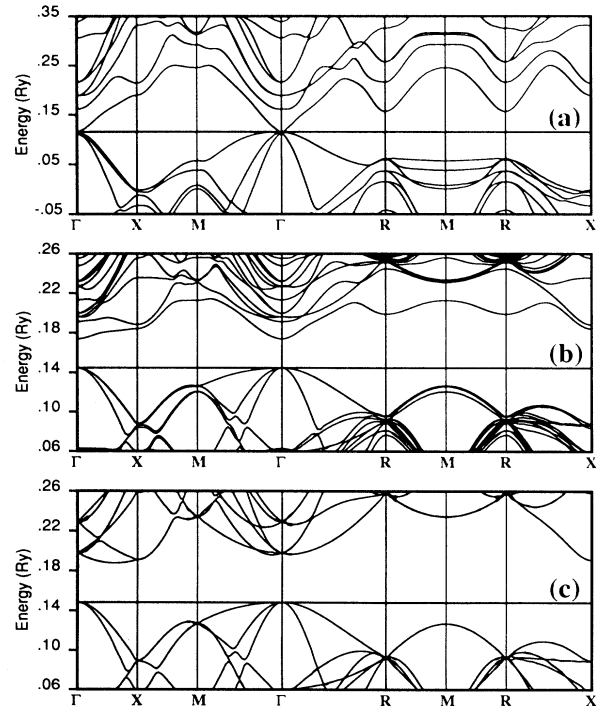


FIG. 2. The band structures for supercells containing (a) 7 Si atoms and a H-B pair, (b) 63 Si atoms and a H-B pair, and (c) 64 Si atoms. The horizontal line in each plot indicates the top of the valence band. For clarity, only a few bands directly above and below the band gap are shown. Notice the different energy scale in (a).

For a relatively small supercell, the effect of the band gap reduction can be severe, as seen in Fig. 2(a) where the band gap virtually vanishes. With increasing supercell size, the impurity density decreases, thus the effect of interactions between the host Si atoms and the impurities as well as among impurities from neighboring supercells should be less drastic. This has indeed been observed, as the calculations using 8-, 16-, 32-, and 64-atom supercells have shown that the band gap increases systematically with the supercell size, and the band structure for the 64-atom supercell resembles that of the pure silicon lattice, as shown in Fig. 2. It should be noted that, with adoption of the LDA, the calculated semiconducting band gap is smaller than the actual value.<sup>30</sup>

Similar dependence of the electronic structure on the supercell size has been observed for the system of Si containing a H-P pair. Figure 3 shows the band structures for 8- and 64-atom supercells. Comparing with that of pure Si [Fig. 2(c)], the band gap for the 8-atom supercell is considerably smaller because of an impurity band rising above the top of the Si valence bands. This effect, artificially introduced with the use of supercells, is significantly reduced in the case of a 64-atom supercell, where a band structure very much like that of a pure Si crystal has been obtained.

The improvement in calculated electronic structures by using larger supercells is reflected in the results for directly measurable physical properties as well. This is demonstrated in Fig. 4, in which the frequency of the H vibration along the H-Si bond (the stretching mode) in a H-Si-P complex has been evaluated for various supercell sizes. The procedure used to derive these frequency values will be discussed in detail in the next section. Comparing with the experimental value,<sup>6</sup> it is observed that the H vibrational frequency is substantially underesti-

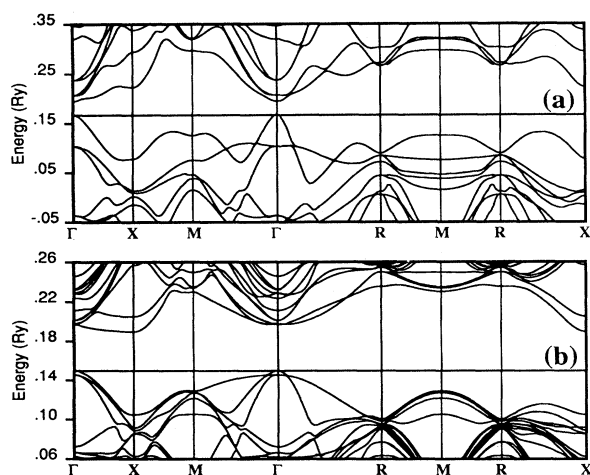


FIG. 3. The band structures for supercells containing (a) 7 Si atoms and a H-P pair and (b) 63 Si atoms and a H-P pair. The horizontal line in each plot indicates the top of the valence band. For clarity, only a few bands directly above and below the band gap are shown. Notice the different energy scales.

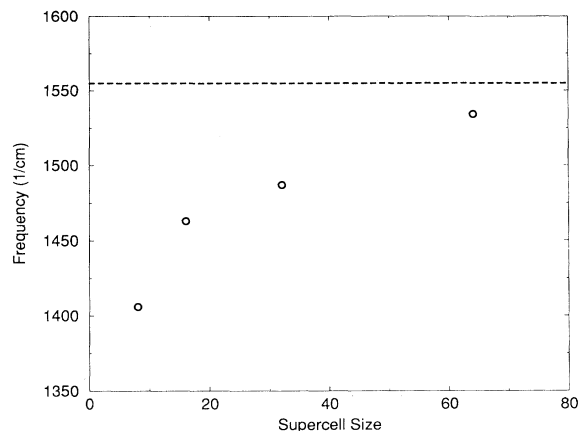


FIG. 4. Frequency of the H-stretching vibration in a H-Si-P complex for various supercell sizes. The dashed line indicates the value obtained from an infrared-absorption experiment (Ref. 6).

ated if using a relatively small supercell. As the supercell becomes larger, the theoretical result converges steadily toward the experimental data. This is understandable since the separation between impurity complexes is determined by the supercell size. Thus by using a large supercell in the study one can better simulate a real system.

Above discussions indicate that previous results obtained using the DFM for Si containing a P-H pair<sup>11-13</sup> or a B-H pair<sup>14,15</sup> can be improved by using a larger supercell and a higher kinetic-energy cutoff. In this work, we adopt a 64-atom supercell and a 22-Ry cutoff, yielding more than 15 000 plane waves in the basis set. The threshold for convergence of the geometry is chosen so that the largest component of the force on each atom does not exceed  $10^{-4}$  a.u. Unless specified otherwise, all calculations are performed using these parameter values.

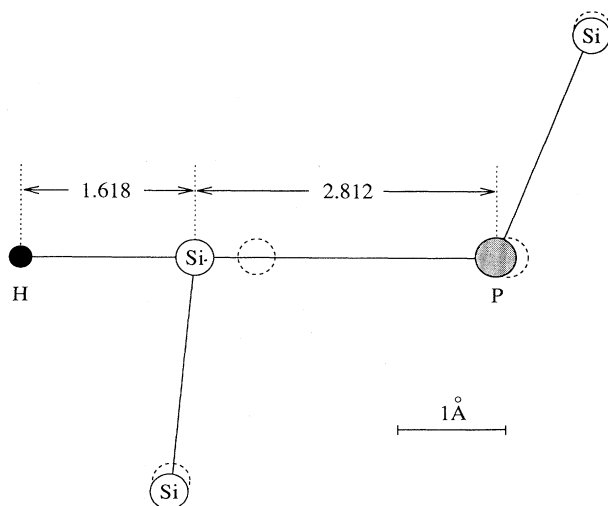


FIG. 5. The equilibrium configuration for the system of H in P-doped Si. The dashed circles indicate unrelaxed positions.

TABLE I. Calculated equilibrium geometries of the H-Si-P complex.  $\Delta\text{Si}$  ( $\Delta\text{P}$ ) is the displacement of Si (P) from its unrelaxed position. “8-atom” and “Present” represent the result obtained using an 8- and 64-atom supercell, respectively. Results from previous DFM studies are also listed for comparison.

Distance	Ref. 11	Ref. 12	Ref. 13	8-atom	Present
H-Si ( $\text{\AA}$ )	1.69	1.66	1.65	1.645	1.618
Si-P ( $\text{\AA}$ )	2.84		2.72	2.883	2.812
$\Delta\text{Si}$ ( $\text{\AA}$ )	0.66	0.59	0.52	0.710	0.557
$\Delta\text{P}$ ( $\text{\AA}$ )	0.18	0.14	0.14	0.178	0.096

In addition, we note that the results shown in Figs. 2, 3, and 4 have been obtained for fully relaxed equilibrium configurations. In the next two sections we shall present the results obtained for Si-H-P and Si-H-B systems.

### III. H-P IN Si

The calculated equilibrium configuration for hydrogen in phosphorus-doped silicon is shown in Fig. 5. The H atom is found at an antibonding site (at the Si side) of a Si-P bond, which is in agreement with most of the previous calculations using the DFM.<sup>11–13</sup> In particular, the obtained structure indicates that P relaxes towards H, contrary to some earlier results from other models.<sup>7,9</sup> Resulted positions of the atoms in the H-Si-P complex are listed in Table I, along with results from other studies using the DFM.

An examination of Table I indicates that all calculations yield qualitatively similar results, namely, a slight P displacement ( $\Delta\text{P}$ ) and a relatively large Si displacement ( $\Delta\text{Si}$ ) from their corresponding unperturbed Si lattice sites towards H, giving rise to a threefold coordinated P atom. Quantitatively, our study shows that  $\Delta\text{Si}$  is 0.557  $\text{\AA}$ , and its three nearest-neighbor Si atoms relax outward by 0.095  $\text{\AA}$ , thus reducing the Si-Si bond length to 2.054  $\text{\AA}$ . The calculated  $\Delta\text{P}$  is 0.096  $\text{\AA}$ , which is lower than the values from previous works by others.

For comparison, in Table I we have also presented the equilibrium geometry acquired using an 8-atom supercell, where not only the value of  $\Delta\text{P}$  (0.178  $\text{\AA}$ ) is comparable to that obtained in Ref. 11, but also H is located at practically the same position very close to a  $T_d$  site. However, a careful study shows that the resulted H-Si distance and  $\Delta\text{Si}$  are systematically reduced with increasing supercell size (for example,  $\Delta\text{Si} = 0.710$   $\text{\AA}$ , 0.660  $\text{\AA}$ , 0.558  $\text{\AA}$ , and 0.557  $\text{\AA}$  for the 8-, 16-, 32-, and 64-atom supercell, respectively), thus moving H away from the  $T_d$  site and closer to the Si-P complex. In the configuration for the

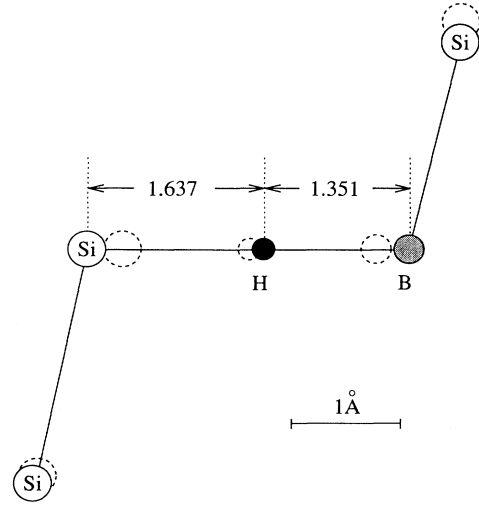


FIG. 6. The equilibrium configuration for the system of H in B-doped Si. The dashed circles indicate unrelaxed positions.

64-atom supercell, the distance between H and the adjacent  $T_d$  site is 0.176  $\text{\AA}$ , a significant departure from the equilibrium structure obtained using an 8-atom supercell and that presented in Ref. 11. Also, it is interesting to note that the systematic reduction of the H-Si distance should play a partial role in the increase of the calculated H vibrational frequency with the supercell size, which has been observed in Fig. 4.

To evaluate the frequencies for the H vibrations in the stretching mode (along the Si-H bond) and wagging mode (perpendicular to the Si-H bond), slight shifts of H along the P-Si-H axis in both directions are imposed while other atoms maintain their positions. The total energies of these configurations are then calculated and fitted to a parabola.<sup>15</sup> These shifts have to be small enough so that the H atom is still within the assumed harmonic range, yet large enough to yield an energy difference that can overcome the resolution of the calculation. Here we selected the shift values to be 2% and 4% of the Si-Si bond length, resulting in a maximum energy change of 43 meV in the stretching mode, which is well above the resolution (approximately 0.2 meV). The derived H vibrational frequency is 1534  $\text{cm}^{-1}$  for the stretching mode, and 847  $\text{cm}^{-1}$  for the wagging mode. In Table II, these results are compared with the data from an infrared-absorption experiment, along with those from other theoretical studies.<sup>11–13</sup> It is seen that they are very similar qualitatively, and the H vibrational frequency values obtained from the current work, among all available DFM

TABLE II. Calculated and measured vibrational frequencies (in  $\text{cm}^{-1}$ ) for the H in a H-Si-P complex.

Mode	Ref. 11	Ref. 12	Ref. 13	Present	Expt. (Ref. 6)
Stretching	1290	1460	1450	1534	1555
Wagging	715	740	720	847	809

TABLE III. Calculated equilibrium geometries of the Si-H-B complex.  $\Delta\text{Si}$  ( $\Delta\text{B}$ ) is the displacement of Si (B) from its unrelaxed position. Results from previous theoretical studies as well as an ion-channeling measurement are also listed for comparison.

Distance	Ref. 7	Ref. 8	Ref. 9	Ref. 10	Ref. 14	Ref. 15	Present	Expt. (Ref. 3)
H-Si ( $\text{\AA}$ )	1.56	1.46	1.44	1.49	1.63	1.65	1.637	
H-B ( $\text{\AA}$ )	1.51	1.59	1.66	1.53		1.36	1.351	
$\Delta\text{Si}$ ( $\text{\AA}$ )	0.16	0.22	0.26	0.16		0.24	0.328	
$\Delta\text{B}$ ( $\text{\AA}$ )	0.55	0.48	0.49	0.47	0.47	0.42	0.310	$0.28 \pm 0.03$

calculations, are in the best quantitative agreement with the experimental data. This is not surprising since the evaluated frequency may have a strong dependence on the supercell size, as discussed in Sec. II, whereas smaller supercells and lower kinetic-energy cutoffs have been used in previous calculations that are shown in Table II.

#### IV. H-B IN Si

For the system of hydrogen in a boron-doped silicon lattice, the H atom is located at the bond-center site of a Si-B bond, as shown in Fig. 6. The converged equilibrium geometry is presented in Table III, together with results from previous theoretical studies. Our result indicates that, in the Si-H-B complex, the H atom is closer to B than to Si. This is in agreement with previous calculations using the DFM,<sup>14,15</sup> whereas the opposite has been obtained in other studies based on the cluster approach.<sup>8-10</sup> Also listed in Table III is the data from an ion-channeling measurement,<sup>3</sup> where the B displacement from its unperturbed substitutional position ( $\Delta\text{B}$ ) has been measured. It is seen that our calculated value for  $\Delta\text{B}$  (0.310  $\text{\AA}$ ) is within the error bar of the experimental data ( $0.28 \pm 0.03$   $\text{\AA}$ ), while other theoretical estimates are considerably larger.

The H vibrational frequency for the stretching mode can be determined following the procedure described in Sec. III. However, more computational effort is needed in order to examine properties of the H wagging-mode vibration in B-doped Si, because the total energy does not vary rapidly as H is shifted from its equilibrium position in directions perpendicular to the Si-H bond. For this reason, to our knowledge there has been no previous attempt using the DFM. We adapt a stringent convergence criterion in this study, so that the resolution of the calculated total energy is improved to approximately 0.04 meV. For a H shift of 0.1  $\text{\AA}$  in directions perpendicular to the Si-H-B axis, an energy increase of 0.9 meV

has been obtained, and two wagging modes are found to be degenerate. Resulted vibrational frequencies for the stretching and wagging modes are shown in Table IV. The predicted wagging-frequency value of 233  $\text{cm}^{-1}$  is substantially lower than that for H in P-doped Si, and it is interesting that no experimental search has been conducted in this low-frequency range.

Our calculation using a 64-atom supercell yields a frequency of 2031  $\text{cm}^{-1}$  for the stretching mode, significantly higher than the experimental data of 1903  $\text{cm}^{-1}$  from an infrared-absorption measurement.<sup>5</sup> This is somewhat surprising, considering the fact that excellent agreement with the experimental data can be achieved by repeating the calculation using an 8-atom supercell with the same 22-Ry cutoff (the resulted frequency is 1897  $\text{cm}^{-1}$ ). However, this quantitative agreement may be a coincidence. A careful examination of Table IV shows that the calculated frequency value increases with the supercell size, which is also consistent with the observation made for the system of H-P pair in Si (see Fig. 4). Therefore, the result obtained using an 8-atom supercell may not be optimal.

The reason for the overestimate of the H vibrational frequency for the stretching mode is not yet understood. We point out, however, the present evaluation of the frequency is based on the curvature of the potential energy surface (PES) at the H equilibrium site, which may be insufficient. A comprehensive study of the vibrational properties requires a full scan of the PES as well as taking into account the coupling to other vibrational modes in the system, which is beyond the scope of this work.

#### V. CONCLUSION

We have examined how the microscopic structures of Si-H-B and Si-H-P complexes obtained from calculations based on the density-functional theory depend on the kinetic-energy cutoff and the supercell size. It is seen that obtained results for the electronic structures and measur-

TABLE IV. Calculated vibrational frequencies (in  $\text{cm}^{-1}$ ) for the H in a Si-H-B complex. “8-atom” and “Present” represent the result obtained using an 8- and 64-atom supercell, respectively. Results from previous DFM studies are also shown for comparison, along with the data from an infrared-absorption measurement.

Mode	Ref. 14	Ref. 15	8-atom	Present	Expt. (Ref. 5)
Stretching	1820	1830	1897	2031	1903
Wagging				233	

able properties vary systematically with increasing impurity separation (i.e., supercell size). Using a 64-atom supercell and a kinetic-energy cutoff of 22 Ry, the equilibrium structures for the systems of hydrogen in boron- and phosphorus-doped silicon crystal are reached by allowing all atoms within the supercell to relax. The results not only further confirm the configurations for the Si-H-B and H-Si-P complexes proposed in other studies, but also show quantitative improvements in most calculated geometry parameters and vibrational properties. In particular, excellent agreement with the experimental data has been achieved for the evaluated B displacement in the Si-H-B structure and for the H vibrational frequency in the H-Si-P system. Also, the calculation yields a fre-

quency of  $233\text{ cm}^{-1}$  for the H wagging-mode vibration in the Si-H-B system which has yet no experimental support. The discrepancy between the estimated value and the measurement for the vibrational frequency of H along the Si-H-B axis requires further study.

#### ACKNOWLEDGMENTS

The authors would like to thank Dale Koelling, Erich Stoll, and Norman Troullier for their contributions. This work was partially supported by the Swiss National Science Foundation. The computation was carried out on the NEC SX/3 at CSCS in Manno, Switzerland.

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