# Ab initio study of silicon in the R8 phase

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We present a detailed *ab initio* study of the electronic and structural properties of the recently discovered *R*8 phase of silicon. Within the framework of density-functional theory in the local-density approximation and using pseudopotentials with a plane-wave basis, we study the energetics of the *R*8 phase compared to the other tetrahedrally bonded diamond,  $\beta$ -Sn, and BC8 phases. The bonding properties and the pressure dependence of the bond lengths of the BC8 and *R*8 phases are investigated. An analysis of the band structure reveals that *R*8 silicon could be a semimetal or semiconductor with a small, indirect band gap. Our computed density of states of *R*8 silicon shows a sharpening of the valence-band edge similar to the one observed for amorphous silicon. [S0163-1829(97)01535-X]

### I. INTRODUCTION

The technological importance of silicon has motivated much work on its high-pressure phase diagram. Upon compression to about 10-12.5 GPa, <sup>1-4</sup> silicon transforms from the diamond structure (Si I) to the metallic  $\beta$ -Sn phase (Si II). When unloaded, it does not convert back to the diamond phase, but assumes the BC8 structure (Si III), a bodycentered cubic phase with an eight-atom basis<sup>1</sup> which is metastable at ambient pressure. Annealing of BC8 silicon produces yet another metastable form of silicon, which is of the hexagonal diamond type<sup>1</sup> (Si IV). On very fast pressure release from 12 and 15 GPa to ambient pressure, two other metastable phases with tetragonal symmetry have been reported<sup>5</sup> (Si VIII and Si IX), although their structure could not be completely determined. At pressures above  $\sim$  13 GPa,<sup>3</sup> the  $\beta$ -Sn phase is distorted to the Imma structure (Si XI),<sup>6</sup> which connects the  $\beta$ -Sn phase continuously with the simple hexagonal Si v observed at  $\sim 16$  GPa.<sup>2,3</sup> When applying even higher pressures, silicon assumes a yet unidentified structure<sup>2,7,8</sup> at  $\sim$  38 GPa (Si VI) before it converts to the hexagonal close-packed Si VII at  $\sim$  42 GPa.<sup>8</sup> Finally, at a pressure of  $\sim$  79 GPa, silicon is found to be in the facecentered cubic structure<sup>7,8</sup> (Si x).

Recently, with silicon XII another metastable phase has been discovered<sup>9,10</sup> and has been named *R*8, because of its rhombohedral lattice with eight atoms in the basis. The present paper will focus mostly on this phase, and discuss its structural and electronic properties in comparison with the closely related BC8 phase. We repeat and extend a previous *ab initio* study by Piltz *et al.*,<sup>10</sup> but find significant discrepancies regarding the zero-pressure volume and energy of *R*8. Attention will be devoted to the density of states (DOS) of the *R*8 phase, as it is the only known crystalline silicon phase with five-membered rings, which have been predicted to affect the electronic properties.<sup>11</sup>

#### **II. STRUCTURES**

All of the structures addressed here have already been described previously.<sup>10,12</sup> Therefore we will focus on those

structural features which are relevant in the present context.

The diamond structure  $O_h^7(Fd3m)$  has a fcc lattice with a two-atom basis at the Wyckoff 8(*a*) positions. Each atom is surrounded by four equidistant neighbors at the corners of a regular tetrahedron. A tetragonal distortion transforms the diamond structure into the  $\beta$ -Sn structure, which has a body-centered tetragonal unit cell [space group  $D_{4h}^{19}(I4/amd)$ ] with a two-atom basis on the 4(*a*) positions. At a pressure of 10.3 GPa, the unit cell parameters are<sup>6</sup> a = 4.665(1) Å, c = 2.572(1) Å. Each atom has four nearest neighbors at 2.42 Å, and two second-nearest neighbors at an only slightly larger distance of 2.57 Å. The angles between the bonds to the four nearest neighbors are 149° and 94°, largely deviating from the ideal tetrahedral angle of 109.47°.

Figure 1 shows the more complex BC8 phase. It has a bcc lattice with an eight-atom basis located at the 16(c) sites, and is classified by the space group  $T_h^7(Ia\overline{3})$ . We can think of the structure as composed of building blocks with the shape of ethane molecules. The crystal structure is obtained



FIG. 1. Ball and stick model for the BC8 phase of silicon. The primitive unit cell for the bcc lattice is shown with bold lines. At its corners, a basis with the shape of a vertically oriented ethane molecule is attached. The two different bond lengths are labeled A and B.

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FIG. 2. Ball and stick model for the R8 phase of silicon. The R8 phase has a rhombohedral unit cell which is a slightly distorted bcc cell. The four distinct bond lengths are labeled A', B', B'', and C. One can go from BC8 to R8 by breaking the central bond of the BC8 basis, and reconnecting it along the dashed lines (labeled A'') with the next basis unit along the c axis, resulting in the C bond.

by attaching this building block to the bcc lattice vertices, oriented in the (111) direction. In Fig. 1 the bcc primitive unit cell is shown, with the basis attached to only four of the eight corners of the unit cell in order to avoid cluttering. Due to the high symmetry of the structure, there is only one internal degree of freedom, which is the parameter  $x_0$  for the atoms at the 16(c) sites. At ambient pressure, it is measured to be<sup>10</sup>  $x_0$ =0.1003(8). Figure 1 also shows the two distinct bond lengths labeled *A* and *B* following Biswas *et al.*<sup>12</sup> At ambient pressure, experiment<sup>10</sup> finds the *A* bond (2.31 Å) to be significantly shorter than the *B* bond (2.39 Å). The angle between two *B* bonds is 117.6°, whereas the *AB* angle is 99.0°. Both angles differ substantially from the ideal tetrahedral angle of 109.47°.

The R8 structure (Fig. 2) is characterized<sup>9</sup> by the space group  $C_{3i}^2(R\overline{3})$ . The angle  $\alpha$  between the basis vectors of the rhombohedral lattice is<sup>10</sup> 110.07(3)°, which brings the lattice very close to the bcc lattice of the BC8 structure, where  $\alpha$ = 109.47°. Due to the reduced symmetry, R8 has four parameters specifying the eight-atom basis. At a pressure of 8.2 GPa they are<sup>10</sup> u = 0.2922(9) for the atoms at the 2(c) site, and x = 0.4597(8), y = -0.0353(7), z = 0.2641(7) for the atoms at the 6(f) sites. Notice that the R8 phase coincides with BC8 if we choose  $\alpha = 109.47^{\circ}$ ,  $u = 2x_0$ , x = 0.5, y = 0, and  $z=0.5-2x_0$ . We label the four distinct bonds of the R8 structure with A', B', B'', and C. A range of bond angles is present. About the 2(c) site, the bond angles are  $117.9^{\circ}$  and 98.5°, whereas the 6(f) atoms are enclosed by bond angles of 92.1°, 93.0°, 103.1°, 105.0°, 114.9°, and 136.8°. The BC8 and R8 phases are related in a simple way, as can be seen from Figs. 1 and 2. To convert from BC8 to R8, one merely has to break the A bond of each BC8 building block, and reconnect it in the opposite direction to form the C bond in the R8 phase (see Fig. 2). We can see that the A' bond of R8 is reminiscent of the A bond of BC8, and likewise B' and B''in R8 correspond to the B bond of BC8. This fact will become important when we compare the structural properties of the two phases. The distance labeled A'' (shown with a thin, dashed line in Fig. 2) originates from a BC8 A bond,



FIG. 3. Enthalpy (in rydbergs) of tetrahedral phases of silicon as a function of pressure (in GPa). The enthalpy is given with respect to the diamond phase. Above 8.5 GPa the  $\beta$ -Sn phase is more stable than the diamond phase. BC8 and *R*8 are both unstable, and have a very similar bulk modulus. At higher pressure, *R*8 is more stable, whereas at lower pressures, BC8 is favored. The calculated transition pressure between  $\beta$ -Sn and BC8 is 7.4 GPa.

but has now become a second-nearest neighbor distance in the R8 phase.

#### **III. METHOD**

Our *ab initio* calculations are done within the framework of density-functional theory (DFT) in the local-density approximation (LDA) using the parametrization of the Ceperley-Alder functional<sup>13</sup> by Perdew and Zunger.<sup>14</sup> The interaction of the valence electrons with the ionic cores is represented with a separable,<sup>16</sup> norm-conserving, nonlocal Troullier-Martins<sup>15</sup> pseudopotential. We expand the wave functions in plane waves<sup>17</sup> up to a cutoff energy of 24 Ry. For sampling the Brillouin zone, Monkhorst-Pack<sup>18</sup> grids of the following sizes are used:  $8 \times 8 \times 8$  for the diamond phase,  $10 \times 10 \times 10$  for  $\beta$ -Sn, and  $6 \times 6 \times 6$  for BC8 and *R*8. With these parameters, the total energy is accurate to better than 0.2 mRy per atom. For all structures considered, the internal degrees of freedom as well as the lattice parameters are relaxed simultaneously with a quasi-Newton method.<sup>19</sup>

## IV. STABILITY OF FOURFOLD COORDINATED PHASES OF SILICON

Figure 3 shows the results of our DFT-LDA total energy calculations. Plotted is the enthalpy difference in Ry per atom with respect to the diamond phase as a function of pressure. When the pressure exceeds 8.5 GPa, the  $\beta$ -Sn phase becomes lower in enthalpy than the diamond phase. Diamond anvil cell experiments find this transition to happen at a pressure of about 10–12.5 GPa.<sup>1-4</sup> The transition pressure we find is in agreement with recent all-electron calculations (8.0 GPa),<sup>20</sup> and other pseudopotential plane-wave calculations [7.8 GPa,<sup>21</sup> 8.4 GPa (Ref. 22)]. Since the experiments only measure the transition pressure to larger values. A more detailed discussion and assessment of the accuracy with which the present theory reproduces this phase transition can be found in Refs. 20 and 21.

A direct  $\beta$ -Sn to diamond transition upon decompression is not observed in experiment, but rather a conversion to the *R*8 phase at pressures of about 8.2–10.1 GPa.<sup>9,10</sup> Our calculations predict this transition at 7.4 GPa.

In experiment,<sup>9</sup> the R8 phase transforms reversibly to the metastable BC8 structure at  $\sim 2$  GPa. From Fig. 3, we can see that the pressure dependence of the enthalpy of the two phases is very similar. Using a fit to the Murnaghan equation of state,<sup>23</sup> we find the bulk modulus of the R8 phase to be 89 GPa, which is close to the 92 GPa we calculate for BC8. The similar bulk moduli and the small differences in volume between the R8 and the BC8 phase make it difficult to determine the transition pressure from our calculation. The enthalpy curves of R8 and BC8 in Fig. 3 cross at -1.9 GPa. However, an inaccuracy of only 1 mRy/atom in our enthalpy calculation would make the computed transition pressure vary by about 9 GPa. The convergence with respect to the k-point mesh for the enthalpy of the BC8 and R8 phases is accurate to 0.05 mRy/atom. When using different pseudopotentials, we see the enthalpy differences between R8 and BC8 vary by 0.15 mRy/atom. Even though a precise determination of the transition pressure is not possible, we note that the qualitative behavior is correct: on decompression  $\beta$ -Sn first transforms to R8, and then to BC8. Despite the small enthalpy differences between the two phases, the transition need not show a large hysteresis. This is because the transformation can be accomplished by breaking only one out of 16 bonds.

The quasi-Newton scheme we use to relax the structure yields information about phonon frequencies at the  $\Gamma$  point.<sup>19</sup> At all pressures, we find the *R*8 and the BC8 to have purely real phonon frequencies and therefore they are locally stable. In other words, there is a persistent energy barrier between the two phases. Therefore the phase transition is of first order, in agreement with experiment.<sup>10</sup> A softening of the optical phonon modes at  $\Gamma$  is not found within the pressure range studied.

## V. STRUCTURAL PROPERTIES OF THE BC8 AND R8 PHASES

In the present section, we will discuss the structural properties of the *R*8 and BC8 phases of silicon, focusing especially on the variation of the structure when external pressure is applied.

In Fig. 4 how the dependence of the crystal lattice parameters of the R8 and the BC8 phase as a function of pressure. The experimental data points are from Piltz et al.<sup>10</sup> We find good agreement between theory and experiment. The phase transition from BC8 to R8 is of first order, and is accompanied by a discontinuous change in volume. Although our calculations yield an overall underestimation of the volume as is typical for LDA calculations,<sup>24</sup> we find good agreement for the volume differences. With respect to the density at the phase transition, we compute the R8 phase to be denser by 1.2%, which is a rather small change, and is close to the 2.1% determined by x-ray diffraction.<sup>10</sup> The agreement is even better if we take into account that, due to the limited x-ray intensity and the few lines observed, the volume of the R8 phase is uncertain by about  $\pm 0.7\%$ . Our findings are in disagreement with previous DFT/LDA calculations,<sup>10</sup> where



FIG. 4. Volume and rhombohedral angle  $\alpha$  of the silicon *R*8 and BC8 phases as a function of pressure. The experimental data points for *R*8 (solid squares) and BC8 (bullets) are from Ref. 10. The theoretical data points (open symbols) for the volume are connected with a fit to the Murnaghan equation of state, whereas for the rhombohedral angle, the line is a guide to the eyes only. The rhombohedral angle of BC8 is fixed by symmetry to be 109.47°.

the jump in volume appears to be about 7%.

The equations of state of BC8 and R8 in Fig. 4 are similar because equilibrium volume and the bulk moduli are similar. This is not unexpected, since BC8 can be obtained from R8 by breaking and reconnecting only one out of 16 bonds. Moreover, both phases have a comparable density and are characterized by distorted  $sp^3$ -type bonding.

Also in agreement with experiment,<sup>10</sup> we find the rhombohedral angle  $\alpha$  to open as the pressure on the *R*8 phase is increased (Fig. 4). By opening  $\alpha$ , the second-nearestneighbor distance *A*" between the atoms on the 2(*c*) sites is decreased, bringing them closer to a five-fold coordination. However, even at a pressure of 8.2 GPa, the calculated second-nearest-neighbor distance is about 30% larger than the nearest-neighbor distance, and the system is clearly fourfold coordinated.

Figure 5 shows the change of the *R*8 internal parameters u, x, y, and z as a function of pressure. Good agreement between theory and experiment<sup>10</sup> is observed for x, y, and z [experiment<sup>10</sup> at 8.2 GPa: x=0.4597(8), y=-0.0353(7), z=0.2641(7)]. The computed u, however, is smaller by 4% than the u=0.2922(9) found in experiment. Within the  $\sim 2-10$  GPa stability range of the *R*8 phase, the variation of the internal parameters is comparable to the experimental uncertainty in the published intensity data,<sup>10</sup> and will be difficult to observe. At elevated pressure, the u parameter related to the second-nearest-neighbor distance A''



FIG. 5. Internal degrees of freedom of *R*8 silicon as a function of pressure. The coordinates of the 2(c) atoms relative to the lattice vectors are (u,u,u), while the 6(f) atoms are located at (x,y,z). The experimental data points (solid squares) are from Ref. 10.

ceases to change, along with the rhombohedral angle  $\alpha$ . This means that upon pressure increase, at lower pressures the second-nearest-neighbor distance decreases strongly to facilitate the volume reduction, while above 10 GPa, it merely reduces according to an isotropic volume scaling.

To get a better understanding of the behavior of the R8 phase under compression, we plot in Fig. 6 the various bond lengths as a function of pressure. Evidently, those R8 bonds which are reminiscent of the BC8 bonds behave like their counterparts. Under pressure, the A' bond of R8 resembles the A bond of BC8, and so do the B' and B'' bonds mimic the B bond. The C bond on the other hand behaves rather differently. Under compression, it changes little while the pressure is below about 10 GPa. In this pressure region, most of the volume reduction is accomplished by diminishing the second-nearest-neighbor distance A''. When reaching higher pressure, this process stops, and the C bond starts to shorten.

## VI. ELECTRONIC PROPERTIES OF THE BC8 AND R8 PHASES

Previously the discoverers<sup>9</sup> of the *R*8 phase pointed out the presence of five-membered rings, and indicated that they should affect the electronic properties of the *R*8 phase.<sup>11</sup> While silicon in the BC8 phase is known to be semimetallic,<sup>25</sup> the electrical properties of *R*8 have not been measured yet. In this section, we will extend the *ab initio* study of the electronic structure done previously.<sup>10</sup>

Figure 7 shows the DFT/LDA band structures of silicon in the *R*8 and BC8 phases at zero pressure with the relaxed structural parameters from our calculation. For ease of com-



FIG. 6. The bond lengths of the R8 and BC8 structures as a function of pressure. The squares indicate R8 bond lengths; the circles mark BC8 bonds. R8 has four distinct bond lengths labeled C (solid line), B' (dotted), B'' (dashed), and A' (long dashed). Also shown are the two bond lengths present in the BC8 phase, labeled A (long dashed) and B (dot-dashed). For labeling of the bonds see Figs. 1 and 2.

parison, both are plotted in the rhombohedral Brillouin zone (BZ) shown in the inset. In agreement with experiment,<sup>25</sup> we find BC8 to be a semimetal, with a direct band overlap of 0.8 eV at the rhombohedral T point, which is the H point in the bcc BZ. Turning to the R8 band structure, we see the most interesting changes occurring around the T point. Here the threefold degeneracy at the top of the BC8 valence band is split into a doublet and a singlet, and no direct band overlap is found for R8. Rather, in the R8 phase there is a small indirect band overlap between the T and L points of about 0.3 eV. This is somewhat smaller than the 0.5 eV found by Piltz et al.<sup>10</sup> It is important to mention that LDA tends to predict too small gaps in most semiconductors. For silicon in the diamond structure, an indirect gap of 0.52 eV is found, compared to 1.17 eV from experiment.<sup>26</sup> An accurate prediction of the metallicity of R8 silicon would require, for instance, a quasiparticle energy calculation.<sup>26</sup> Thus, although we find R8 silicon to be a semimetal, it could well be a small-gap semiconductor. However, due to the distinct topology of the Fermi surfaces, the temperature dependence of the electrical resistivity due to electron-phonon scattering should be different.

Model calculations on the tetrahedrally bonded fictitious ST12 phase of silicon with five-membered rings have revealed a number of interesting properties<sup>11</sup> of the density of states. The most striking feature is a sharpening of the valence-band edge, as is seen in amorphous silicon. In Table I we list the ring count for the diamond, BC8, and *R*8 structures. On the average, an *R*8 atom is participating in  $3\frac{3}{4}$  five-membered rings. We show in Fig. 8 the DOS for BC8 and *R*8 as computed within LDA, using the relaxed structural parameters from our calculation. It is interesting to see that indeed the DOS of *R*8 (solid line) shows a sharper valence-band edge than that of BC8 (dashed line). With respect to BC8, apparently weight is transferred from the high peak at -2.3 eV (region 2) to the top of the valence band



FIG. 7. Band structure of silicon in the R8 phase (top graph) and the BC8 phase (bottom graph). The structural parameters are from our calculation at zero pressure. To facilitate comparison, both band structures are plotted along special lines in the rhombohedral BZ. Note the characteristic differences in the vicinity of the T point.



FIG. 8. Density of states per unit cell, per spin, and per eV for silicon in the R8 (solid line) and BC8 (dashed line) phase. For both, the relaxed geometry from our calculation at zero pressure is assumed. The energy is given with respect to the Fermi level. Note the sharper valence-band edge (region 3) of R8, and the less pronounced peak in region 2.

(region 3) at around -1.5 eV. The peak at -2.3 eV has been attributed<sup>11</sup> to the wurtzitelike eclipsed tetrahedral units present in BC8. In fact, when *R*8 is formed from BC8 by the rebonding process discussed earlier, eclipsed tetrahedral units involving the 2(c) atoms get converted into strongly distorted staggered diamondlike configurations.

To gain a better understanding of some of the features in the R8 DOS, we examine the charge density contributions from the states in regions 1-3 marked with boxes in Fig. 8. We find the states in region 1 to be more localized between the 2(c) atoms, where they form an *s*-type bond. This is also evident from the local and angular-momentum resolved DOS shown in Figs. 9 and 10 for the 2(c) and 6(f) atoms, respectively. There, the peak in region 1 is stronger on the 2(c)than on the 6(f) site, and has mainly s character. Region 3, on the other hand, is predominantly p type, and the states here also have most of their amplitude between the 2(c)atoms. This is consistent with our examination of the charge contributions originating from states in region 3. To make sure this is not an artifact of using the LDA-relaxed structure, we repeated our analysis using the experimental structural parameters for R8 at 8.2 GPa, but aside from minor changes due to the different pressure, the features are the same. In summary, the characteristic differences in the DOS

TABLE I. The number of five-, six-, and eight-membered rings per atom is shown in the last three columns. Seven-membered rings are absent in all of the structures considered here. The R8 phase is the only one with five-membered rings. There, each 2(c) atom is included in twice as many five-membered rings as a 6(f) atom.

Structure	Atoms/cell	5-memb.	6-memb.	8-memb.
Diamond	2	0	12	24
BC8	8	0	9	36
2(c) atom of R8	2	6	3	21
6(f) atom of R8	6	3	5	25
R8 (average)	8	$3\frac{3}{4}$	$4\frac{1}{2}$	24



FIG. 9. Local density of states per unit cell, per spin, and per eV for the 2(c) atoms of R8 silicon. The radius of the integration spheres is chosen such that for the shortest bond they just touch. Also shown is the local projection onto angular momentum eigenfunctions with *s* (dotted line), *p* (dashed line), and *d* (dot-dashed line) character. The characteristic features of R8 in regions 1 and 3 are strongly pronounced.

of BC8 and R8 are visible in the local DOS of both the 2(c) and 6(f) sites, but are more pronounced for the 2(c) atoms.

It is not clear whether the sharpening of the valence-band edge (region 3) can be directly associated with fivemembered rings. However, the local DOS of the 2(c) atoms shows this feature stronger than the 6(f) atoms, while at the same time there are twice as many five-membered rings running through the 2(c) sites than through the 6(f) sites (Table I). Perhaps it is more intuitive to interpret the sharpening of the valence-band edge as a result of the distortion from the ideal tetrahedral angle, leading to high-energy *p*-type states at the top of the valence band, and low-energy *s*-type levels at the valence-band bottom.

### VII. CONCLUSION

In our *ab initio* DFT/LDA calculation, we find the energetics and unit cell volume of the *R*8 phase of silicon very similar to the one of the BC8 phase. This is reflected in their similar bulk modulus of 89 GPa (*R*8) and 92 GPa (BC8), and makes it difficult to compute the transition pressure between these two phases. At higher pressures, *R*8 becomes more stable than BC8, in agreement with experiment.<sup>9</sup> Both BC8 and *R*8 are found to be metastable with respect to the diamond or  $\beta$ -Sn structure. They are separated by a finite-energy barrier over a large pressure range, and thus the BC8 $\rightarrow$ *R*8 phase transition is of first order.

With increasing pressure, the rhombohedral angle  $\alpha$  of the



FIG. 10. Same as in Fig. 9, but for the 6(f) atoms of R8. The *s*-type peak in region 1 and the *p*-type peak in region 3 are similar to the ones seen for the 2(c) atoms, but less pronounced.

R8 phase opens, thereby reducing the second-nearestneighbor distance to accommodate the volume reduction. Our calculated lattice parameters and the internal degrees of freedom x, y, and z of the R8 phase agree well with the available experimental data, but our u parameter comes out to be 4% smaller.

The LDA band structure shows R8 silicon to be a semimetal with a 0.3 eV indirect band overlap between the T and the L points. This is different from BC8, where a direct band overlap of 0.8 eV is found at the T point. Due to the inaccuracies of LDA band structures, R8 silicon could also be a semiconductor with a small, indirect gap.

Similar to amorphous silicon, the DOS of R8 shows a sharpening of the valence-band edge in R8 silicon. The states right at the edge are dominantly p type, and have more weight on the 2(c) sites. A strong peak in the BC8 DOS, which has been attributed before to wurtzite-type eclipsed configurations,<sup>11</sup> is less pronounced in R8. This coincides with the disappearance of eclipsed configurations when BC8 is transformed to R8.

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