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First-principles pseudopotential study of the structural phases of silicon

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A first-principles pseudopotential study of 11 phases of silicon is reported: diamond (cd), body-centered cubic (bcc), face-centered cubic (fcc), body-centered tetragonal (bct), simple hexagonal (sh), hexagonal-close-packed (hcp), double-hexagonal-close-packed (dhcp), simple cubic (sc), β-tin, a body-centered cubic structure with eight atoms per unit cell (bc8), and a simple tetragonal structure with 12 atoms per unit cell (st12). For each structure and for each volume considered we have minimized the energy with respect to all structural degrees of freedom. We have used large basis sets and very careful integrations over the Brillouin zone to resolve the small energy differences between structures, and our pseudopotentials incorporate nonlinear core exchange-correlation corrections, leading to more accurate results than those of previous calculations. We find good agreement with experiments and with some previous calculations but a few discrepancies remain and we gain some insights into the high-pressure phase diagram of silicon.

I. INTRODUCTION

While the diamond structure of silicon is the most widely studied of all semiconductors, there have also been a number of experimental and theoretical studies of the high-pressure phases of silicon.[1-7] A detailed picture of the phase diagram of silicon has emerged, although a number of unanswered questions remain. Experimental studies have used the diamond-anvil technique,[8] which can achieve pressures of at least 2500 kbar, together with energy dispersive x-ray-diffraction techniques which give information about the structures formed. A large number of theoretical studies have been performed using the first-principles pseudopotential total-energy method,[9-16,52,62] although other studies have also been reported using a self-consistent linear combination of atomic orbitals (LCAO) technique;[17] the linearized-muffin-tin-orbital (LMTO) method, with[18,19] and without[20] shape approximations to the potential; and a generalized-pseudopotential-theory (GPT) method.[18]

Experimentally it is well established that silicon in the diamond structure (known as Si-I) transforms to the metallic β-tin structure (Si-II) at pressures of about 100–125 kbar.[1-4] The stability range of the β-tin phase is now known to be quite small. Until recently it was thought that β-tin Si transformed into the simple hexagonal phase (Si-V) at about 130–165 kbar,[2-4] although it has been recently found that an intermediate phase, denoted *Imma* after its space group, is formed in this pressure range.[7] The simple hexagonal phase is stable up to pressures of around 380 kbar, whereupon a transformation to a presently unidentified phase known as Si-VI has been observed.[2,6] This phase was originally assigned to the double-hexagonal-close-packed structure,[5] which consists of a stacking of hexagonal-close-packed layers intermediate between that of hexagonal-close-packed and face-centered-cubic, but this assignment is now known to be incorrect.[6] Si-VI transforms to the hexagonal-close-packed structure (Si-VII) at about 420 kbar,[2,5,6] which in turn transforms to the face-centered-cubic phase[21] at about 790 kbar.[5,6] The phase is stable up to the highest pressures so far attained of about 2480 kbar.[6]

In addition to the stable high-pressure phases of silicon, a number of metastable phases have been produced by releasing pressure under different conditions.[3,4,22-26] A fourfold coordinated structure with a body-centered-cubic unit cell containing eight atoms, known as the bc8 or Si-III phase, has been recovered as a metastable phase after releasing pressure from the β-tin phase.[3,4,22-24] The bc8 structure has also been obtained by a similar procedure for germanium,[27] where it is known as Ge-IV. Very recently it has been reported[26] that the β-tin phase of Si does not transform directly into the bc8 phase, but instead transforms via an intermediate rhombohedral phase called $r8$.[21] The rhombohedral phase undergoes a reversible transition to bc8 Si at a pressure of 20 kbar.[26] Another structure known as st12, which has a simple tetragonal unit cell containing 12 atoms, has also been formed under pressure release from β-tin Ge,[27-30] although this phase has not been reported in silicon. The st12 structure is also fourfold coordinated, but the bond angles are highly distorted from the perfect tetrahedral angles, and it has the rather unusual topological feature of odd-membered rings. Whether one obtains bc8 Ge or st12 Ge under pressure release from β-tin Ge depends on the conditions of pressure release. Recent experiments have indicated that germanium brought rapidly to ambient pressure from 140 kbar transforms into the bc8 phase, whereas the st12 phase is favored under slower decompression.[27] In the case of silicon the bc8 phase is obtained under slow decompression from the β-tin phase,[3,4,22,26] and two other fourfold-coordinated phases with large tetragonal unit cells (named Si-VIII and Si-IX by the authors of Ref. 25) have been obtained under rapid decompression.[25] These phases have space groups $P4_12_1$ and $P4_22$, respectively, but the positions of the atoms within the unit cells are not known. Heating and recrystallization of bc8 Si produces the hexagonal diamond structure[24,22] (known as Si-IV), in which the layers are stacked in the wurtzite manner. (Small regions of wurtzite stacking may also be induced in diamond structure silicon by nanoindentation.[31]) The hexagonal diamond structure is known to be very slightly higher in energy than cubic diamond structure silicon (calculated to be about 0.01 eV per atom).[14,32]

The aim of this work is to produce a highly accurate set of results from the first-principles pseudopotential method for the energies of structural phases of silicon. We have calculated the energies of the diamond (cd), β-tin, simple hexagonal (sh), hexagonal-close-packed (hcp), double-hexagonal-close-packed (dhcp), face-centered-cubic (fcc), body-centered-tetragonal (bct), simple cubic (sc), body-centered-cubic (bcc), bc8, and st12 phases of silicon. The results of previous calculations have often been subject to inaccuracies due to the use of inadequate basis sets and poor Brillouin-zone integrations. In this study we have taken great care to make sure that such numerical errors are very small, and we believe that our study is the most complete and accurate published to date.

There are a number of unresolved issues concerning the phase diagram of silicon; for example, the structure of the stable phase Si-VI is still completely unknown. In addition there are discrepancies, some of them serious, between the various theoretical calculations and between the theoretical and experimental results. The calculations reported in this study have enabled us to draw several conclusions about the high-pressure phase diagram of silicon.

The rest of the paper is organized as follows. In Sec. II we summarize the main features of our calculations. In Sec. III we give a short account of the construction of the zero-temperature phase diagram. A discussion of the results concerning the relative stability of the phases and their structures under pressure is presented in Sec. IV. Concluding remarks are made in Sec. V.

II. FIRST-PRINCIPLES PSEUDOPOTENTIAL CALCULATIONS

The first-principles pseudopotential method has been applied to a wide range of systems, generally giving good agreement with experimental results. An excellent review of this method and applications of it has been given in the recent article by Pickett.[33] In this section we give only the computational details pertaining to the present calculations.

Our calculations are for periodic crystals. The potentials and wave functions were expanded in a plane-wave basis set containing all waves up to 24 Ry in energy, and the resulting matrix equations were solved using an iterative diagonalization technique.[34] We used the Ceperely-Alder form[35] of the local-density approximation (LDA) for the exchange-correlation energy. Scalar relativistic corrections were included in the manner of Kleinman,[36] incorporating the relativistic exchange corrections proposed by MacDonald and Vosko.[37] We neglected spin-orbit splitting, which can be included within this framework, but which adds significantly to the computational effort while having only a very small effect for silicon. The first-principles norm-conserving pseudopotential[38] used to represent the Si^{4+} ions in our calculations was constructed using the scheme due to Kerker.[39] We also incorporated the nonlinear core exchange-correlation corrections introduced by Louie, Froyen, and Cohen,[40] which improve the transferability of the pseudopotential.

Integrations over the Brillouin zone were performed by sampling on regular grids of points in reciprocal space using the method of Monkhorst and Pack.[41] These integrations need to be very accurate because the energy differences between phases are small. We have carried out a careful study of the size of grid required, and have concluded that grids containing many more **k** points should be employed than used in many previous calculations. For the semiconducting diamond phase only a relatively small number of **k** points is needed, but for the metallic phases many more **k** points are required to resolve the Fermi surface. The numbers of **k** points used in the current study for each of the 11 structures considered are listed in Table I. To ensure comparable accuracy for calculations on different metallic phases, the number of **k** points used should be roughly proportional to the volume of the Brillouin zone (BZ), which is inversely proportional to the number of atoms in the unit cell. For the metallic phases we have used approximately 8000 **k** points for structures with one atom per unit cell, 4000 **k** points for structures with two atoms per unit cell, etc. To account for the Fermi structure we have used the Gaussian occupation scheme of Fu and Ho,[42] with the modification of Ref. 43. In each case a Gaussian of width 0.05 eV was used.

We have also tested the effects of basis set truncation on our results, which we believe to be very small with the 24-Ry cutoff used for all the results presented in this paper. The effect of the 11.5-Ry cutoff used in the pioneer-

TABLE I. The total number of **k** points and the irreducible number of **k** points used in the calculations for each phase of silicon. The number of atoms in the unit cell is also given.

Structure	**k** points in the whole BZ	**k** points in the irreducible BZ	Atoms in the unit cell
cd	512	60	2
st12	64	6	12
β-tin	3920	1050	2
sh	7776	1080	1
hcp	3888	540	2
fcc	8000	770	1
bc8	1000	64	8
bcc	8000	250	1
dhcp	1944	270	4
sc	8000	220	1
bct	8000	1155	1

ing work of Yin and Cohen[9] was to introduce a systematic bias in the energies whereby energies calculated at small volumes per atom are shifted upwards in energy with respect to those at larger volumes. We believe that the errors introduced by the truncation of the basis set and the finite resolution of the **k** point sampling have been rather underestimated in previous studies. After extensive tests we believe that in the present calculations the energy differences between phases are converged to better than about 0.005 eV per atom. We have also tested the effects of the nonlinear core exchange-correlation corrections. The most significant effect is that for a given volume the pressure is increased by about 10 kbar, which, for instance, changes the equilibrium lattice constant of cd Si from 5.382 Å (without core corrections) to 5.400 Å (with core corrections); i.e., moves it toward the experimental value of 5.429 Å.[44] Although the incorporation of nonlinear core corrections undoubtedly improves the quality of our calculations, we do not believe that they are particularly important in silicon, even at the compressed volumes considered in our study.

Several of the structures that we have considered have internal degrees of freedom. The β-tin, bct, hcp, dhcp, and sh phases have a single degree of freedom, which we take to be the c/a ratio. The bc8 structure also has a single internal degree of freedom, while the st12 structure has five. (Full descriptions of the bc8 and st12 structures are given in Refs. 45 and 13.) For each structure and each volume considered, a full minimization with respect to all degrees of freedom was performed, using the calculated values of the forces on the atoms and the stress tensor.[46] For the more complicated st12 phase, a steepest descents algorithm was used to locate the structure with minimum energy.

III. CONSTRUCTION OF THE PHASE DIAGRAM

The total energies per atom for each structure as a function of volume were fitted to Chebyshev polynomial series of degree 4–6, depending on the number of data points available for each phase. The number of points in the fits varies from 8 to 15, and in each case the fit is good, with an estimated error of less than 10^{-4} eV per atom. To investigate the phase stability at zero temperature we require the enthalpy H as a function of pressure, p, where

$$H = E + pV \; . \tag{1}$$

The pressure was calculated by direct differentiation of the Chebyshev series, and the values so obtained are in excellent agreement with those calculated from the stress theorem.[46]

In Fig. 1 we plot the energies per atom, E, against the volume per atom, V, for the 11 phases considered. The high-pressure region in Fig. 1 is very congested, and for clarity we give an enlargement of this region in Fig. 2. Such plots have normally been given in theoretical studies of high-pressure phases, and therefore they allow for comparisons to be made with previous studies. However, the relative stability of the phases is best illustrated by the enthalpy-pressure plot of Fig. 3, which will be discussed in detail in Sec. IV. For clarity we plot the difference in enthalpy between each phase and the bcc phase. The most stable phase at any given pressure is the one with the lowest enthalpy.

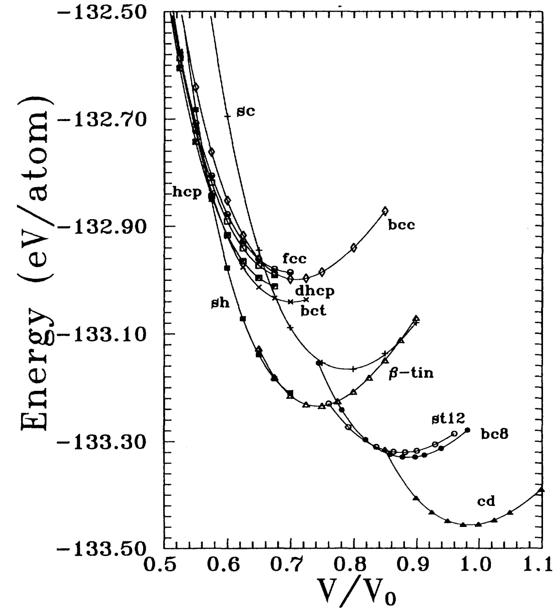

FIG. 1. The energy E in eV per atom vs the volume V for the 11 phases under consideration. The volume is given in terms of the reduced volume V/V_0^{exp}, where $V_0^{\text{exp}} = 20.024$ Å^3 per atom is the experimental equilibrium volume of cd-Si. The different symbols indicate our theoretical values, and the lines are fits to these data.

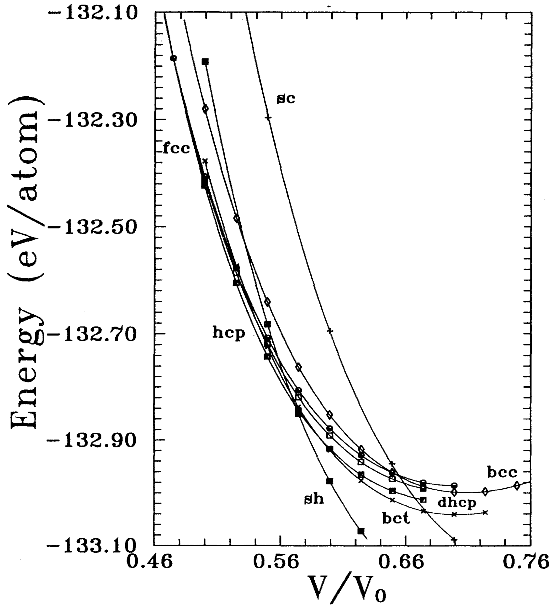

FIG. 2. As in the previous figure, but showing more detail of the high-pressure region.

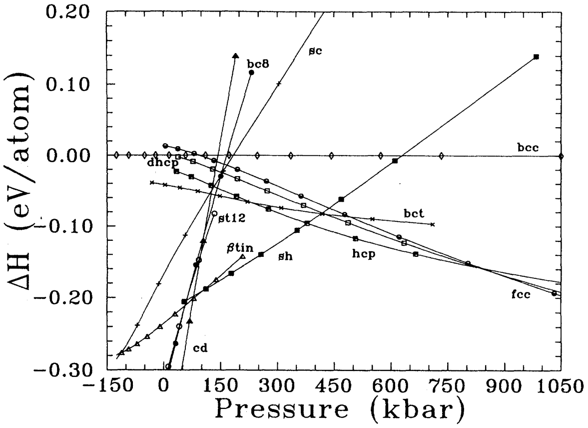

FIG. 3. The enthalpy H in eV per atom vs the pressure p in kbar for 11 phases of silicon. The enthalpy is plotted with respect to that of the bcc phase.

IV. RESULTS

A. Relative stability of the phases

The enthalpy-pressure plot of Fig. 3 shows that the following sequence of phase transitions is predicted with increasing pressure: cd→β-tin→sh→hcp→dhcp→fcc. The transition pressures and volumes corresponding to the calculated sequence of transitions are given in Table II. This sequence differs from the experimentally observed one in three ways; we have not studied the *Imma* phase between β-tin and sh in detail, or the Si-VI phase of unknown structure between sh and hcp, and we have found a very small range of pressures at which dhcp is stable between hcp and fcc. In fact the enthalpy curves for fcc, hcp, and dhcp are so close in the region 800–850 kbar that the small region of stability for the dhcp phase may be due to small residual inaccuracies in the calculations. The *Imma* phase has been reported experimentally in Ref. 7 and has been theoretically studied in detail in Ref. 16 by Lewis and Cohen, who found that it actually lies at slightly lower energies than both the β-tin and the sh structures, except at very compressed volumes. The existence of such a phase is not completely unexpected, since similar structures have previously been found to be stable at high pressure for InSb and GaAs.[47,48] Moreover, both the β-tin and sh structures can be thought of as particular cases of the body-centered-orthorhombic *Imma* structure for which the so-called u internal parameter takes the values $\frac{1}{8}$ and $\frac{1}{4}$, respectively, and the two axial ratios are no longer independent but are related by $b/a=c/a$ (β-tin) and by $b/a=\sqrt{3}c/a$ (sh). Lewis and Cohen[16] found that a stable *Imma* phase exists with a structure intermediate between the β-tin and sh structures. We have performed just two calculations for this structure using (a) the experimental values of the structural parameters given in Ref. 7, and (b) the values calculated by Lewis and Cohen[16] by relaxing the structure at the same volume. In our calculation the latter set gives a slightly lower energy than the former, which lies below the curves for both the β-tin and sh structures on Fig. 1.

TABLE II. Calculated transition pressures p_t for each of the transitions I→II and the corresponding volumes of each phase, V_t^{I} and V_t^{II}. We also include the hcp→dhcp and dhcp→fcc transitions (see text).

	p_t (kbar)	V_t^{I} (Å^3/atom)	V_t^{II} (Å^3/atom)
cd→β-tin	78	18.361	14.013
β-tin→sh	102	13.796	13.581
sh→hcp	377	11.877	10.999
hcp→fcc	843	9.545	9.404
hcp→dhcp	830	9.575	9.476
dhcp→fcc	874	9.374	9.332

The calculated pressure for the cd→β-tin transition of 78 kbar is significantly lower than the experimental results of about 103 kbar due to McMahon and Nelmes,[7] 113±2 kbar due to Hu *et al.*,[4] 117 kbar by McMahon *et al.*,[49] and 125 kbar given by Jamieson,[1] although it is plausibly close to the value of 88 kbar quoted by Olijnyk *et al.*[2,50] Calculations of the cd→β-tin transition pressure in silicon have yielded a variety of results over the years, although modern calculations support a transition pressure close to ours. The recent pseudopotential calculations of Boyer *et al.*[15] gave a value of 84 kbar. In addition, a very recent pseudopotential calculation by Moll *et al.*[51] obtained a cd→β-tin transition pressure of 80 kbar. We believe that the lower value of about 80 kbar is now firmly established as the LDA prediction for the cd→β-tin transition pressure in Si. A similar state of affairs holds for germanium. We had previously reported the LDA value of the cd→β-tin transition pressure in Ge to be 60 kbar.[52] We have now repeated these calculations with the same accuracy as the present study of silicon, and have obtained a more accurate value of 74 kbar. We note that this value is very close to the transition pressure of 75 kbar obtained by Kresse and Hafner,[53] who used similar calculational methods to ours. The two calculated values are significantly lower than the commonly accepted experimental value of about 105 kbar.[54,55]

The consistency between the various modern theoretical values of the cd→β-tin transition pressures in Si and Ge shows that the results are not sensitive to the precise details of the calculations such as the scheme used for generating the pseudopotential, etc. The reasons for the discrepancies between the calculated and experimental transition pressures in Si and Ge are unclear at the present time. The cd→β-tin transition involves considerable bond breaking and the reverse β-tin→ cd transition is severely hindered by kinetic factors, which make it difficult to estimate the actual equilibrium transition pressure. Depending on the conditions of pressure release, the metastable fourfold-coordinated structures known as bc8 and st12 are formed.[22,27,28,30] Consequently the higher experimental values for the cd→β-tin transition pressure may be due to kinetic effects. Besson *et al.*[56] discussed the problems inherent in determining equilibrium transition pressures from experimental data, and suggested that the accepted diamond–zinc-blende→metallic phase transition pressures in group-IV and III-V semiconductors should be revised downwards. On the other hand it is also possible that the LDA is not accurate for determining the energy difference between semiconducting and metallic phases, or that it is inaccurate when the volume difference between the phases is large, as is the case with this transition.

The calculated pressure for the β-tin→sh transition of 102 kbar is significantly lower than the experimental values of 132±2 kbar,[4] and about 160 kbar (Ref. 2) for the onset of the formation of the sh structure. Our value is also smaller than the previously calculated value of 143 kbar,[11] but is reasonably close to the more recent value of 120 kbar.[10,14] As can be seen in Fig. 1, the enthalpy curves of the β-tin and sh phases are very close, and very small inaccuracies in the energies can result in a significant shift in the transition pressure. The existence of the intermediate *Imma* phase, which we have not considered in detail, will further increase the calculated pressure for formation of the sh structure.

Although a sh→hcp transition was reported in early experimental investigations,[4] it is now well established that this transition does not occur directly, and that the intermediate phase Si-VI, of unknown structure, is stable in the pressure range of 380–420 kbar.[2,6] In early work,[5] Si-VI was tentatively assigned to the dhcp phase, although this identification was later established to be incorrect when higher-resolution x-ray data were obtained.[6] Our results confirm that dhcp is *not* a stable phase in this pressure range, as it is about 0.02 eV per atom higher in enthalpy than the hcp phase. This value is in good agreement with the pseudopotential result mentioned in Ref. 57. Our calculated value of 377 kbar for the sh→hcp transition should be considered as an upper bound for the stability of sh Si, which is consistent with the experimental facts.

We have found a very small region of stability for the dhcp phase in the pressure range 830–874 kbar, between the hcp and fcc phases. The bonding in hcp, dhcp, and fcc (and all other poltypic stackings of close-packed layers) is very similar and, consequently, the enthalpy curves are very nearly parallel (see Fig. 3). The enthalpies of hcp, dhcp, and fcc are almost identical at a pressure of about 850 kbar, and it is not possible to determine whether or not the small range of stability of the dhcp phase is a consequence of very small inaccuracies in the calculations. The energies and enthalpies of different polytypic stackings of layers can be expressed in terms of interlayer interactions. If we use a model for the enthalpy which includes *only* interactions between nearest-neighbor and next-nearest-neighbor layers, it is possible to distinguish between the hcp, dhcp, and fcc phases. This model has been shown to give an excellent description of the energies of SiC polytypes.[58] A property of the model is that when the enthalpies of the hcp, dhcp, and fcc stackings are equal, then all possible polytypes have the same enthalpy. Therefore we predict that at pressures of about 850 kbar the enthalpy required to create a stacking fault in polytypes of close-packed silicon layers vanishes.

Our value for the hcp→fcc transition pressure of 843 kbar is close to the experimental value of 790±20 kbar,[6] and also close to the GPT and LMTO results of Ref. 18. A considerably larger transition pressure of 1160 kbar was obtained in a previous pseudopotential study.[14] The discrepancy between this higher value on the one hand, and the all-electron and experimental results on the other hand, led the authors of Ref. 6 to suggest that core relaxation effects, which are not included in pseudopotential calculations, are important at these compressed volumes. Our more accurate pseudopotential results show that this evidence must now be disregarded.

In the pressure range of 380–420 kbar in which Si-VI is stable, we find that sh (eightfold coordinated), bct (essentially tenfold coordinated with a c/a ratio of about 0.8), and hcp, dhcp, and fcc (twelvefold coordinated) have very similar enthalpies. This interesting observation suggests that the phase Si-VI, which has a large unit cell, may contain silicon atoms with a variety of coordination numbers anywhere between eight and twelve.

We also note a theoretical study in which a metallic fivefold-coordinated body-centered-tetragonal phase was considered,[15] which the authors found to be metastable and thought might be manufactured by a process involving the application of anisotropic stress. It should be noted that the body-centered-tetragonal phase studied by these authors is not the same as the bct phase that we have studied, which is essentially tenfold coordinated. Boyer *et al.*[15] found that cd Si becomes unstable to their fivefold-coordinated phase at a pressure of 126 kbar. However, inspection of Fig. 3 shows that cd Si is unstable to many other phases at similar or lower pressures: β-tin (78 kbar), bc8 (106 kbar), st12 (98 kbar), sh (79 kbar), sc (127 kbar), bct (125 kbar), hcp (129 kbar), dhcp (136 kbar), and fcc (140 kbar). Kinetic barriers between metallic phases are expected to be smaller than between semiconducting and other phases. Therefore there seems to be no good reason why one should expect that "once in this phase it could well be stable at ambient conditions," as claimed by Boyer *et al.*[15]

Our values for the energy differences between the cd, sc, bcc, and fcc phases are much closer to the full-potential LMTO (FP-LMTO) results of Methfessel, Rodriguez, and Andersen[20] that to the original pseudopotential results of Yin and Cohen.[9] For example, we obtain an energy difference between the cd and bcc phases at zero pressure of 0.46 eV per atom, which is significantly closer to the FP-LMTO result of 0.43 eV per atom[20] than to Yin and Cohen's value of 0.53 eV per atom.[9] The major difference between our calculations and those of Yin and Cohen are that they used a 11.5-Ry plane-wave basis set cutoff and a small number of **k** points for the Brillouin-zone integrations for the metallic phases, and that they used the Wigner formula[59] for the exchange-correlation energy whereas we use the more accurate Ceperley-Alder expression.[35] However, our calculations locate the β-tin phase at significantly lower energies than in the FP-LMTO calculations.[20] In view of the good agreement for the other phases (at more compressed volumes) it is not likely that this discrepancy is due to the use of a pseudopotential in our calculations. We note that because of its crystal structure the β-tin phase is particularly difficult for the FP-LMTO method,[60] and we suspect that their results for this phase are inaccurate.

We now consider the metastable fourfold-coordinated bc8 and st12 phases. The structures of bc8 and st12 are quite complex, and are discussed in detail in Refs. 13 and 45. The bond angles in bc8 and more especially st12 are significantly distorted from the perfect tetrahedral value, and the packing densities are larger than in the diamond structure at the same pressure. Full details of our bc8 and st12 calculations will be published elsewhere,[61] together with a comparison with the corresponding phases of germanium. Recently we published a study of the bc8 and st12 phases of germanium,[52] showing that both phases are almost degenerate in energy and that both are less stable than either cd Ge or β-tin Ge. Subsequently a study by Crain *et al.*[62] found a much smaller energy difference between cd Ge and the bc8 and st12 phases than in our calculations,[52] and they claimed that st12 Ge is actually a stable phase over some range of pressures. We have carried out comprehensive tests on our germanium calculations, and are completely satisfied that no region of stability of st12 Ge exists. One motivation for carrying out the present calculations on the bc8 and st12 phases of silicon was to test whether our results agreed with those of Crain *et al.*,[62] and in fact we find quite good agreement with their results in this case.

From Fig. 3 we see that both bc8 Si and st12 Si are less stable than either cd or β-tin Si at all pressures, and can therefore be formed only as metastable phases. This is consistent with bc8 being observed under slow decompression of the β-tin phase.[3,4,22] At zero pressure the bc8 phase is 0.126 eV per atom higher in energy than cd Si, while st12 Si is 0.136 eV per atom higher in energy than cd Si. These energy differences are to be compared with the values obtained by Crain *et al.*[62] of 0.110 and 0.118 eV per atom, respectively. The result for bc8 Si is also in good agreement with the earlier pseudopotential result of Biswas *et al.*[13] of about 0.120 eV per atom. For bc8 Si the calculated zero-pressure volume of 17.724 Å^3 per atom is in good agreement with the experimental values of 18.26±0.04 Å^3 per atom[23] and 18.13±0.08 Å^3 per atom.[4] Our calculated value of the x internal parameter of 0.1022 at zero pressure is in reasonable agreement with the old experimental value of 0.1003±0.0008,[23] and is in excellent agreement with the most recent experimental value of 0.1025.[26] Our value of the x parameter is also in good agreement with previous calculated values.[12,13,62] The bulk modulus of the st12 phase is calculated to be 0.82 Mbar, which is a little smaller than the value of 0.96 Mbar [cf. the experimental value of 0.98 Mbar (Ref. 63)] for cd Si, as was found previously for germanium.[52] The calculated bulk modulus of bc8 Si of 0.91 Mbar is intermediate between that of cd Si and st12 Si.

B. Variation of the structural parameters with volume

We now turn our attention to the variation of the c/a ratios with volume for the β-tin, sh, bct, hcp, and dhcp phases, and to the variation of the x internal parameter of bc8, which are plotted in Figs. 4(a)–4(f), respectively, together with various experimental data.

For the β-tin phase we find that the c/a ratio decreases with increasing pressure (decreasing volume). Our values are close to the calculated values of 0.55 (Ref. 10) and 0.551 (Ref. 14) at a volume of 16.0 Å^3 per atom, and are in extremely good agreement with the experimental values of 0.550±0.002 at a volume of about 14.2 Å^3 per atom,[4] and 0.550 at a volume of 14.0 Å^3 per atom.[49] We believe that the value obtained by Needs and Martin[11] of 0.525 at a volume of 13.5 Å^3 per atom is inaccurate, probably because of an inadequate number of points used in the Brillouin-zone integration. We have found that the c/a ratio is rather sensitive to the quality of the Brillouin-zone integration used. Even with the large number of **k** points that we have used, the uncertainty in the c/a ratio of the β-tin phase is about 0.002. The trend observed for the pressure dependence of the c/a ratio is in good agreement with the calculation of Ref. 16. β-tin Si is stable over only a small range of pressures, and we could not locate any experimental data for the volume dependence of the c/a ratio of β-tin Si with which to compare our results.

For the sh phase we find that the c/a ratio increases with decreasing volume, in agreement with the trend seen in the experimental data.[4] This agreement is considerably better than for previous calculations, which gave values of the c/a ratio which are too large. Chang and Cohen[14] obtained a value of 0.955 at a volume of 13.5 Å^3 per atom, which is significantly larger than both our calculated value of 0.940 and the experimental values of 0.937±0.005 (Ref. 3) and 0.936±0.005.[4] Needs and Martin[11] obtained a similar volume dependence to that of Fig. 4(b), but with the c/a ratios approximately 0.015 larger than in the present calculations. Our results for the pressure dependence of the c/a ratio are again in good agreement with the theoretical results of Ref. 16.

The bct phase has not been observed experimentally in silicon, although it has been obtained in tin where it is formed as a high pressure stable phase with a c/a ratio of about 0.91.[64] For silicon we obtain a c/a ratio of about 0.80, which increases with decreasing volume. With a c/a ratio close to 0.80 each atom is approximately tenfold coordinated. At the larger volumes considered, the structure is very soft to changes in the c/a ratio, which makes it quite difficult to obtain accurate values.

For hcp Si we find that the c/a ratio initially increases with decreasing volume down to about 11.0 Å^3 per atom, while at smaller volumes the c/a ratio decreases. The hcp phase is initially formed at a volume of just less than 11.0 Å^3 per atom, and at this volume our value of the c/a ratio of 1.697 is in good agreement with the experimental value of 1.700.[2,6] The data of Duclos, Vohra, and Ruoff[6] indicate that as the volume is further decreased the c/a ratio decreases much more rapidly than predicted by our calculations, although error bars in the experiment are certainly significant. The experimental value of Hu *et al.*[4] for the c/a ratio at about 11.0 Å^3 per atom of 1.64±0.02 is much smaller than both our calculated values and the other experimental values. In Ref. 6 it is suggested that this experimental value is indeed inaccurate, and arises from an overestimation of the a parameter. The present calculation lends support to this suggestion. We also note a similar disagreement concerning the p versus V data measured by Hu *et al.*[4] for the sh and hcp phases, while for the β-tin phase the agreement with other experimental studies is remarkably good. Our value of the c/a ratio at 11.0 Å^3 per atom is in very good agreement with the theoretical result of Chang and Cohen.[14]

The dhcp phase has not been observed experimentally in silicon, and we could not locate any previous calculations of the volume dependence of its c/a ratio. We find that the c/a ratio decreases with decreasing volume, and tends toward the ideal value of 1.633.

The x internal parameter of bc8 Si increases with decreasing volume, as was found for bc8 Ge,[52] and in agreement with other pseudopotential calculations.[62] No experimental data for the variation of x with pressure exist. Our zero-pressure value is in excellent agreement with the experimental values.

C. Equation of state

Although it is most common to compare calculated transition pressures and volumes with experimental values, there is actually much more information than this in the experimental data. Furthermore, the comparison between calculated and experimental transition pressures and volumes is not straightforward because of the complex kinetic factors involved in the transitions. This implies that an analysis based solely on equilibrium thermodynamics may be misleading; however, a proper theoretical treatment of these kinetic factors has not yet been achieved. A fuller comparison between the calculated and experimental results, which is valid even when kinetic factors are important in the transition, can be made by comparing the pressure-volume relation or equation of state for *each* of the phases. In Fig. 5 we plot the reduced volume of the various phases against the pressure for pressures up to 400 kbar, while in Fig. 6 we plot the same quantities, but for the pressure range from 400 to 2500 kbar. For the theoretical data we give two curves: the solid lines are plotted in terms of the theoretical zero-pressure volume per atom of cd Si of 19.686 Å^3 per atom, and the dashed lines are plotted in terms of the experimental zero-pressure volume of 20.024 Å^3 per atom.[44] For the experimental data (various symbols) the reduced volume is defined in terms of the experimental zero-pressure volume per atom of cd Si.

Some scatter is apparent in the experimental data plotted in Figs. 5 and 6, even for data obtained by the same

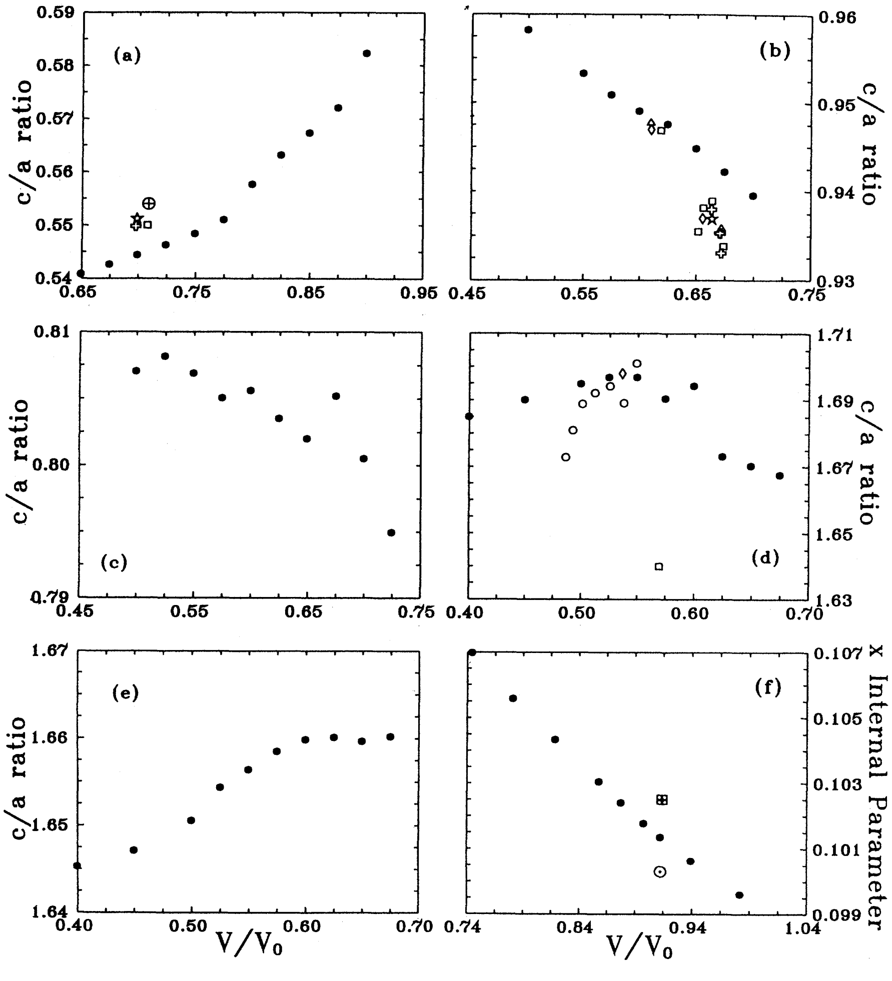

FIG. 4. The calculated c/a ratio for the β-tin (a), sh (b), bct (c), hcp (d), and dhcp (e) structures; and the calculated x internal parameter for the bc8 structure (f) as a function of the reduced volume V/V_0^{exp}, where $V_0^{\mathrm{exp}} = 20.024$ Å^3 per atom is the experimental equilibrium volume of cd-Si. The filled circles correspond to our calculated values and the open symbols correspond to experimental data taken from different sources: triangles—Ref. 3; squares—Ref. 4; diamonds—Ref. 2; circles—Ref. 6; stars—Ref. 54; crosses—Ref. 49; circle with cross—Ref. 1; circle with dot—Ref. 23; square with cross—Ref. 26.

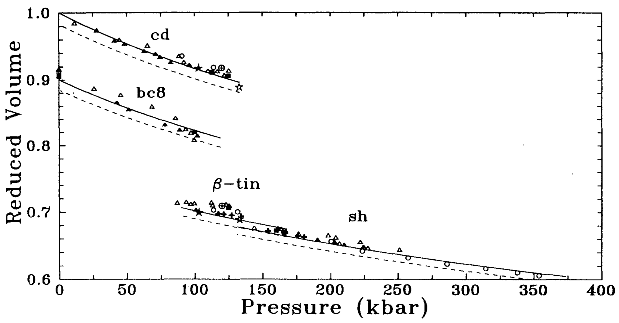

FIG. 5. The reduced volume against pressure for observed phases in the pressure range up to 400 kbar. The experimental data and the dashed theoretical curves are normalized to the experimental zero-pressure volume of the cd-Si structure V_0^{exp} of 20.024 Å^3 per atom, while the solid theoretical curves are normalized to the theoretical zero-pressure volume of cd-Si V_0^{the} of 19.686 Å^3 per atom. The sources for the experimental data are as follows (see text for further details): filled and open triangles—Ref. 3; filled squares —Ref. 4; open squares—Ref. 23; open circles—Ref. 2; crossed circles—Ref. 1; filled stars—Ref. 7; open stars—Ref. 54; filled crosses—Ref. 49. Filled symbols correspond to synchrotron x-ray-diffraction data.

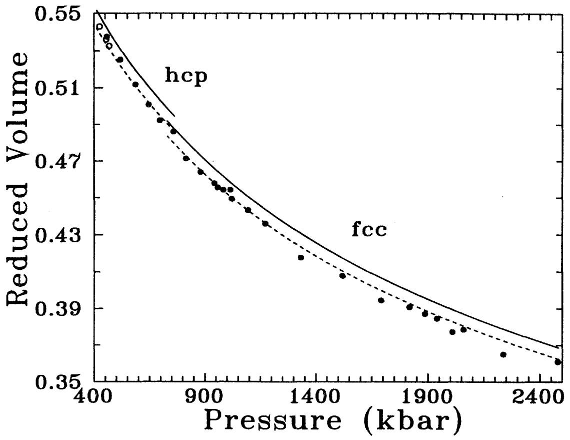

FIG. 6. As previous figure but for the pressure range 400–2500 kbar. Filled circles—Ref. 6; open circles—Ref. 2.

authors, because of the use of different x-ray sources and other experimental conditions. The interested reader should consult the original references for more details and for estimates of the experimental error bars. In Figs. 5 and 6 the filled symbols represent synchrotron x-ray-diffraction data obtained from various references, and the open symbols represent data obtained from other x-ray sources. We have not distinguished data measured on the upstroke from those measured on the downstroke.

The most obvious point to make about Figs. 5 and 6 is that for either definition of the reduced volume the agreement between the calculated and experimental data is good over the entire pressure range. For the phases plotted in Fig. 5 the agreement between the calculated and experimental curves is better for the solid line (normalized to the theoretical volume), and this is especially true when comparing with synchrotron data. For the highly compressed hcp and fcc phases plotted in Fig. 6 the agreement between the calculated and experimental curves is better for the dashed line (normalized to the experimental volume). By construction the theoretical solid curve should coincide with the experimental data for the diamond structure at zero pressure, but the agreement is remarkably good over the entire pressure range of Fig. 5. For the hcp and fcc phases, which are stable at high pressures and correspondingly small volumes, the agreement between the calculated dashed curves normalized to the experimental volume and the experimental data is very good, and is better than the agreement between the solid curves and experiment. The implication of these results is that the LDA calculations are more accurate for the highly compressed and close-packed hcp and fcc phases than for the lower-pressure phases which have more open structures and larger volumes per atom. This conclusion is consistent with the trend observed in a recent quantum Monte Carlo study of the nitrogen atom, dimer, molecular solid, and atomic solid,[65] which showed that the LDA results improve with increasing homogeneity and increasing electron density.

V. CONCLUSIONS

We have performed a first-principles pseudopotential study of 11 phases of silicon. Full minimization of the energy with respect to all structural degrees of freedom has been performed, and we have taken great care to ensure that our results are numerically accurate. The calculated pressure for the cd→β-tin transition is significantly lower than measured values, as has been found previously for germanium. In the pressure range in which the phase of an unknown structure named Si-VI is stable, we find that phases with eightfold, tenfold, and twelvefold coordination are very close in enthalpy. This may be an important observation because it suggests that Si-VI could contain atoms with a variety of different coordination numbers. We predict that the enthalpy required to create a stacking fault in polytypes of close-packed silicon layers vanishes at a pressure of about 850 kbar. In contrast to earlier pseudopotential results our value for the hcp→fcc transition pressure is in excellent agreement with the experimental data. The agreement between our calculated p-V curves and the experimental data is remarkably good, and we have found some evidence that the LDA results are more accurate for the highly compressed close-packed structures than for the phases formed at lower pressures.

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