Transition from β-tin to simple hexagonal silicon under pressure

Richard J. Needs

Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
and Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

Richard M. Martin

Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
(Received 5 June 1984)

Recently a simple hexagonal phase of Si has been discovered at ~130–160 kbar of pressure. We have performed self-consistent density-functional calculations on the β-tin and simple hexagonal structures of Si, using the calculated stress tensor to determine the c/a ratios as a function of volume. We find the simple hexagonal phase to be stable at pressures above 143 kbar. As the two structures are simply related by small strains and displacements of the atoms, we calculate the total energy along a path between the transition structures showing that any barrier between them is lower than 0.01 eV per atom.

A new metallic phase of Si with a simple hexagonal structure containing one atom in the unit cell has recently been discovered to be stable under pressure.[1,2] This structure has not been found in any other element but has been observed in some alloys of tin[3,4] and the In-Bi system.[5] The β-tin structure, which is the well-known[6] high-pressure phase of Si that has been studied theoretically,[7] is found to be stable only over a small range of pressures.[1,2] In this paper we present calculations of the total energy and stress[8] which determine the transition pressure and structural parameters and show that there is a continuum of low-energy structures which encompass both phases.

In the simple hexagonal (sh) structure each atom has six neighbors in the basal plane at a distance a and two neighbors above and below the plane at a distance c. The coordination is effectively eight since $(c/a)_{sh} \sim 1$.[1,2] There are threefold and fourfold rings of atoms, i.e., 60° and 90° bond angles. The existence of this structure is an important finding for our knowledge of the properties of group IV elements since it establishes that these geometries exist at low energy and may be important in cases such as surfaces, the liquid, etc. The competing β-tin structure has a centered tetragonal unit cell with a two-atom basis and a single parameter $(c/a)_\beta$. In the experimental structure there are four nearest and two next nearest neighbors at a slightly greater distance giving ~ sixfold coordination. Thus, Si exhibits an increase in effective coordination number from $4 \rightarrow 6 \rightarrow 8$ with increasing pressure. Furthermore, there is a simple relation between the β-tin and sh structures which is illustrated in Fig. 1, following Refs. 3 and 4. By moving the atoms in the faces of the cell by $c/4$ in the c direction of β-tin, accompanied by the small strains of the cell shown, the lattice becomes simple hexagonal. The symmetry of the intermediate structures obtained by such a continuous transition is orthorhombic.[3,4]

In the present study calculations of the total energy and stress were performed with an *ab initio* norm-conserving pseudopotential[9] in the local density-functional formalism,[10] using the Wigner approximation to the exchange and correlation energy.[11] The resulting Schrödinger equation was solved self-consistently in momentum space at 40 points in the irreducible part of the Brillouin zone for β-tin and 60 points for the sh structure. The total energy[12] and stress

tensor[8] were calculated using a momentum space representation. Plane waves of up to 12 Ry in energy were included in the basis set. With these parameters we estimate convergence in the energy differences between phases ~ 0.01 eV per atom.

Calculations were performed at eight volumes for β-tin and nine volumes for the sh structure. At each volume two preliminary calculations were performed with different c/a ratios close to the minimum in energy. By linear extrapolation of the anisotropic part of the stress ($\sigma_{zz} - \sigma_{xx}$ where z is in the c direction and x is in the a direction) we calculate the c/a ratio at which the stress is isotropic, corresponding to the minimum in total energy at that volume. The residual anisotropy in the stress is typically less than 2 kbar. The total energies from calculations performed at the predicted
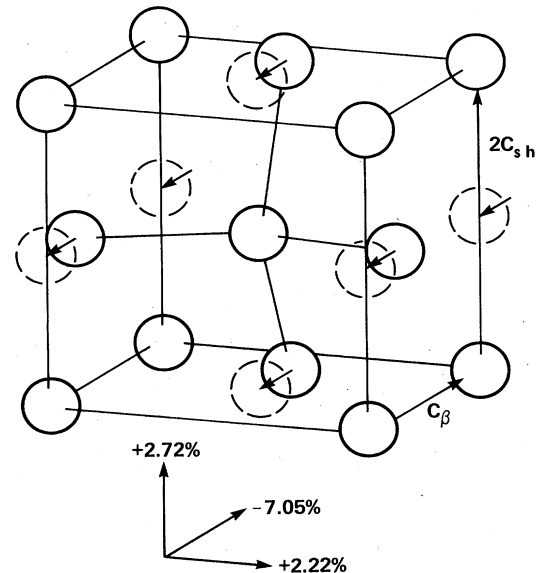

FIG. 1. Atomic positions of β-tin (solid lines) and sh (dashed lines). The strains of the cell required to take the structure between the calculated transition structures are shown. c_β and c_{sh} show the directions of the c axes.

minima are plotted in Fig. 2 together with a curve for diamond Si of comparable accuracy.

The total energies were fitted to Murnaghan's equation of state,[13] shown as solid lines in Fig. 2. The β-tin $\rightarrow$ sh transition pressure, the bulk modulii and their pressure derivatives obtained from these fits and the volumes and c/a ratios of the transition structures are shown in Table I. The transition pressure from diamond to β-tin of 70 kbar is rather lower than the experimental value of $\sim$ 125 kbar (Ref. 14) and also somewhat lower than the value of 99 kbar from the calculations of Ref. 7. The value of 125 kbar is not within the numerical uncertainty of our calculation. This error may be due to the use of the local density approximation in our calculation. We also note that there is a wide variation in reported transition pressures[2] and that hysteresis and temperature dependence may complicate the comparison between theory and experiment.

The β-tin to sh transition is calculated to occur at $\sim$ 143 kbar. This is in excellent agreement with the experimental value of between 130 and 160 kbar.[1,2] However, we must note that if the sh curve were shifted in energy by ~ 0.01 eV per atom relative to β-tin the transition pressure would change by ~ 50 kbar. The transition volumes given in Table I are within 5% of the experimental results obtained from the figures of Refs. 1 and 2.

The c/a ratio of the sh structure is plotted against volume in Fig. 3. The volume dependence of the c/a ratio is appreciable, and we find that it increases with the application of pressure in agreement with Ref. 1. In comparison to the experimental[1,2] c/a ratio of 0.94 close to the transition, we find $c/a \sim 0.957$ (see Ref. 15). Close to the transition to sh we find $(c/a)_\beta \sim 0.525$, slightly below the experimental value of 0.552.[14] The c/a ratio is only weakly dependent on volume—at a volume of 16.0 Å^3 we find $(c/a)_\beta \sim 0.5264$.

Weaire and Williams[16] have noted that the Ewald energy

TABLE I. The β-tin $\rightarrow$ sh transition pressure, the bulk modulus B and its pressure derivative B' from fits of the total energies to Murnaghan's equation of state. The volumes and c/a ratios of the calculated transition structures are also given.

	β-tin	sh
Pressure (kbar)	143	143
B (Mbar)	1.19	1.06
B'	4.01	4.86
Volume (Å^3)	13.553	13.227
c/a	0.525	0.957

of a simple hexagonal lattice is a minimum at a c/a ratio of 0.928 and have used this fact to explain why the c/a ratios of various alloys of tin lie close to this value. Yin and Cohen[7] have argued that the Ewald term is also dominant in determining the c/a ratio of β-tin Si, finding it to be a minimum at $c/a \simeq 0.5445$. We note that with increasing pressure the c/a ratio of the sh structure moves further from the Ewald minimum.

We have also calculated the total energy at five points along a path between the calculated transition structures of β-tin and sh, as described in Fig. 1. We have arbitrarily chosen each of the four parameters describing the path (three dimensions of the cell and the position of the atoms in the faces of the cell) to change linearly between their values at the end points. Since the transition occurs under conditions of constant external pressure the appropriate energy along the transition path is the sum of the internal energy E and the work done against the external forces $P_t \Delta V$, where P_t is the transition pressure and ΔV the change in volume. The enthalpy $H = E + P_t \Delta V$ is the same at the end points of a transition between structures at constant pressure. The intermediate values indicate whether there are stable or metastable phases intervening or if there is a large energy barrier to the transition. Along our path we calculate H to be a constant within the convergence of the energy differences between phases of ~ 0.01 eV per atom. We
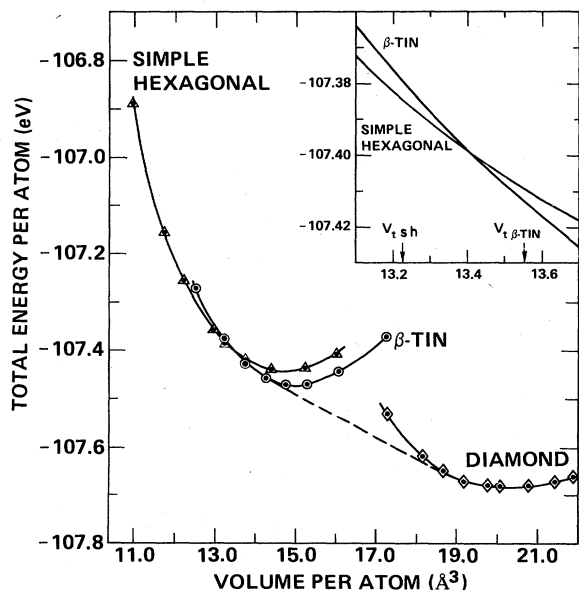

FIG. 2. Energy of the β-tin, sh, and diamond phases. The points indicate calculated energies and the solid lines fits of these energies to Murnaghan's equation of state. The dashed common tangent indicates the transition from diamond to β-tin. The inset shows the region of the transition from β-tin to sh in detail.
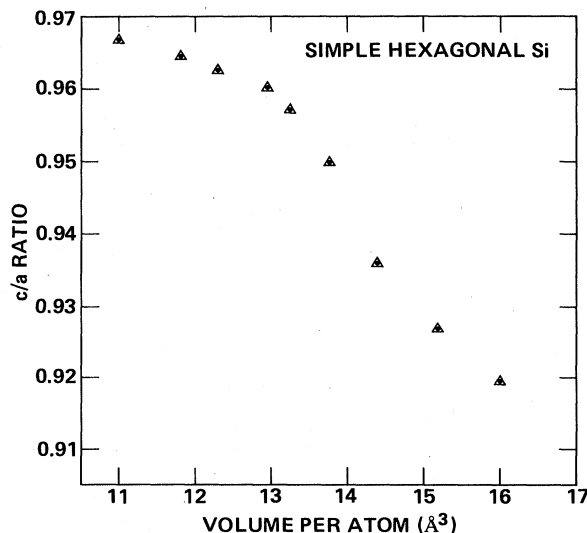

FIG. 3. Calculated c/a ratio of sh Si as a function of volume.

conclude that if a barrier is present it is smaller than 0.01 eV and that the continuum of structures along the path are potentially stable phases.

It is interesting to speculate on the possible consequences of the result that near the transition Si is very soft and has almost constant enthalpy for a range of structures between β-tin and simple hexagonal. Firstly, the phonons in each phase may be very soft. We have shown this by calculating the frequency of the optic phonon shown in Fig. 1 in the β-tin phase to be 87 cm^{-1} at the transition, i.e., a restoring force smaller than that of the optic mode in ordinary Si by a factor of $(520/87)^2 \sim 36$. This low frequency suggests a large temperature dependence of the transition. Furthermore, the soft phonon and the proximity to the transition could enhance superconductivity. It could be interesting to extend previous studies at high pressure which have shown that Si is a large critical field superconductor with $T_c \sim 7$ K.[17] Secondly, the properties are expected to be sensitive to small changes, such as defects and impurities, and may be varied by alloying.

The sh structure has not been found in Ge up to applied pressures ~ 500 kbar.[1] This seemingly large difference between Ge and Si could be explained by only a small change to the energy versus volume curves for Ge from those we have calculated for Si. If the sh curve was shifted to 0.06 eV higher energy we would calculate a transition pressure of over 500 kbar. Such a shift might be due to the differing amount of d character of the wave functions in the two structures. The d occupation in the sh phase near the transition is found to be $\sim 6\%$ higher than that in β-tin.

This is calculated from the difference in the projections of the wave functions onto the d symmetry nonlocal potential which is strongly localized around each atomic site. As Ge has a filled $3d$ core the d pseudopotential is more repulsive in Ge than Si and the d orbitals are moved to larger radii and higher energy with respect to the p orbitals. Thus, at compressed volumes structures with considerable d character are moved to higher energies in Ge compared to Si. This effect is clearly seen in the study of the structures of Si and Ge of Ref. 7. Nevertheless, it is very likely that the overall characteristics of the continuum of structures near stability will persist in Ge and Si-Ge alloys.

In summary, we find a stable simple hexagonal phase of Si at pressures above ~ 140 kbar in good agreement with experiment.[1,2] Using calculations of the stress we have minimized the total energy with respect to the c/a ratios of both phases, which is important when considering the very small energy differences between them. Calculations of the total energy along a path between the two phases show an entire family of structures which are near stability. Any barrier that might exist is found to be less than 0.01 eV per atom.

[1]H. Olijnyk, S. K. Sikka, and W. B. Holzapfel, Phys. Lett. 103A, 137 (1984).
[2]J. Z. Hu and I. L. Spain, Solid State Commun. 51, 263 (1984).
[3]G. V. Raynor and J. A. Lee, Acta Metall. 2, 616 (1954).
[4]B. C. Giessen, Adv. X-Ray Anal. 12, 23 (1969).
[5]B. C. Giessen, M. Morris, and N. J. Grant, Trans. Metall. Soc. AIME 239, 883 (1967).
[6]J. Donohue, The Structures of the Elements (Wiley, New York, 1974).
[7]M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5668 (1982).
[8]O. H. Nielsen and R. M. Martin, Phys. Rev. Lett. 50, 697 (1983); and (unpublished).
[9]D. R. Hammann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979). The Si pseudopotential of G. B. Bachelet, H. S.

Greenside, G. A. Baraff, and M. Schlüter [Phys. Rev. B 24, 4745 (1981)] was used.
[10]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, ibid. 140, A1133 (1965).
[11]E. P. Wigner, Phys. Rev. 46, 1002 (1934).
[12]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979).
[13]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. 30, 244 (1944).
[14]J. C. Jamieson, Science 139, 762 (1963); 139, 845 (1963).
[15]Calculations with 140 points in the irreducible part of the Brillouin zone indicate that the 60 point calculations overestimate the c/a ratio by ~ 0.01 but we expect the volume dependence of the c/a ratio to be well described by the 60 point calculations.
[16]D. Weaire and A. R. Williams, Philos. Mag. 19, 1105 (1969).
[17]J. Wittig, Z. Phys. 195, 215 (1966).