Rapid Communications

Theoretical study of high-pressure orthorhombic silicon

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(Received 18 August 1993)

Ab initio calculations of the structural properties of a recently discovered body-centered orthorhombic phase of Si are presented. This high-pressure phase (denoted *Imma* after its space group) was observed at pressures between the transition pressures for the β-Sn and simple hexagonal (sh) phases of Si. Total-energy calculations indicate that the optimal *Imma* structure varies with cell volume from the β-Sn structure at large volumes to the sh structure at small volumes when all three structures are described in terms of the *Imma* unit cell. The energy of the *Imma* phase is found to be lower than or equal to the energies of the β-Sn and sh phases for all cell volumes.

A recent angle-dispersive x-ray diffraction study by McMahon and Nelmes[1] of Si at high pressure reports an intermediate structural phase at pressures between the transition pressures for the β-Sn and simple hexagonal (sh) phases. Although the high-pressure properties of Si have been widely investigated both theoretically and experimentally,[2] until now Si was thought to transform directly from the β-Sn structure to the sh structure at about 16 GPa. In particular, a previous x-ray diffraction study[3] interpreted the diffraction pattern between 13.2 and 16.4 GPa as resulting from a mixture of the β-Sn and sh phases, with the transformation completed by 16.4 GPa. However, McMahon and Nelmes[1] are unable to fit their data to any such mixture. Instead, they index the diffraction pattern to a body-centered orthorhombic lattice with space group *Imma* which is a generalization of both the β-Sn and sh structures. This structure (denoted *Imma*) is the monatomic equivalent of the proposed structure for high-pressure compound phases of InSb II (Ref. 4) and GaAs III (Ref. 5).

Previous theoretical studies have considered the possibility of an intermediate orthorhombic phase between the β-Sn and sh phases,[6,7] although not in detail. In Ref. 6, the total energy was calculated for five structures along a linear, *Imma*-based path from β-Sn to the sh structure. It was found that within the resolution of their calculation ($\sim$0.7 mRy/atom) the continuum of structures along this path were viable candidates for stable phases. The authors of Ref. 7 suggested that an accurate calculation of the energy barrier between the β-Sn and sh phases would involve varying several structural parameters. Their suggested structural variations are equivalent to exploring the *Imma* structure.

This article reports on a first-principles investigation of the structural properties of the proposed orthorhombic phase of Si and its relative stability compared to both the β-Sn and sh structures. The energy of the orthorhombic phase is found to be lower than or equal to the energy of both the β-Sn and sh phases for all unit cell volumes. For small (large) volumes the *Imma* and sh (β-Sn) structures are comparable in energy, whereas for intermediate volumes the energies of all three structures are distinct. Similar behavior is found in the volume dependence of the optimal structural parameters (i.e., axial ratios and internal parameters) of the *Imma* phase. For very large volumes, the *Imma* structural parameters approach the values that give the β-Sn structure. As volume decreases, the optimal *Imma* structure gradually deviates from the β-Sn-like structure and approaches the sh structure. At very small volumes (high pressure), the *Imma* and sh structures are nearly identical. This calculated trend in the *Imma* structure from a β-Sn-like phase to a sh-like phase accounts for the changes seen in the x-ray diffraction pattern[1] upon compression.

The overall agreement between the calculations and the measurements of Ref. 1 is excellent. In particular, calculated structural parameters for the three phases agree with reported experimental values to within 0.5% (and in some cases much better) for axial ratios and a few percent for internal parameters. For the reference volume (13.6 Å^3) at which the diffraction pattern for the *Imma* phase was indexed, calculations show that the *Imma* structure is distinct from and lower in energy than both the β-Sn and sh phases. This is consistent with the observed x-ray data.

Figure 1 shows schematically the structure of the *Imma* phase, with open and filled circles referring, respectively, to the two Si atoms of the basis. This structure has a body-centered orthorhombic Bravais lattice with space group *Imma*. Its two-atom primitive cell is defined by lattice vectors $\mathbf{a}_1 = \frac{1}{2}(a, b, -c)$, $\mathbf{a}_2 = \frac{1}{2}(-a, b, c)$, and $\mathbf{a}_3 = \frac{1}{2}(a, -b, c)$, and atomic positions $\tau_{\pm} = \pm[\frac{1}{4}\mathbf{a}_1 + (\frac{1}{4} + u)\mathbf{a}_2 + u\mathbf{a}_3]$, where u is an internal
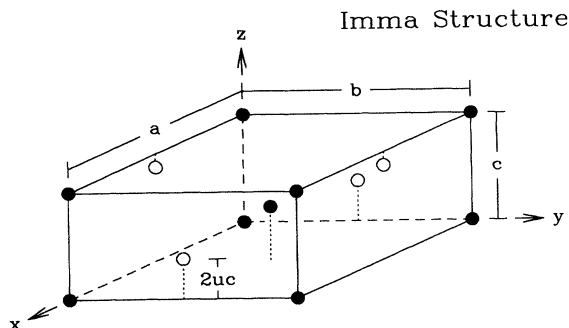
Imma Structure

FIG. 1. Schematic representation of the body-centered orthorhombic *Imma* structure. Open and filled circles correspond to the two Si atoms of the basis, respectively. Dotted lines serve only to show atomic positions. See the text for a thorough description of the *Imma* structure.

parameter (varying from $\frac{1}{4}$ to $\frac{1}{8}$) which determines the relative z coordinate of the two atoms in the basis. The three parameters b/a, c/a, and u specify the structure for a given cell volume. In practice, b/a is slightly less than or equal to unity, and c/a is slightly larger than $\frac{1}{2}$.

The *Imma* structure is a generalization of the β-Sn and sh structures in that they both can be described by the *Imma* unit cell with specific restrictions on the structural parameters. In particular, the two parameters u and b/a are restricted by symmetry for both the β-Sn and sh structures, leaving only c/a as a free variable. The β-Sn structure is body-centered tetragonal with a two atom basis, and is given by the *Imma* structure with $b/a = 1$ and $u = \frac{1}{8}$. The simple hexagonal structure is obtained from *Imma* by setting $u = \frac{1}{4}$ and $b/a = \sqrt{3}\,c/a$. The resulting sh cell is not the conventional primitive cell but is related to it in the following way: if primed letters denote axes of the conventional sh cell and unprimed letters denote *Imma* axes, then $c' = \frac{1}{2}\,a$ and $a' = c$. Thus, the *Imma* cell is rotated with respect to the conventional sh cell and is twice the size.

Calculations are performed using the *ab initio* pseudopotential total energy method in a plane-wave basis.[8-10] In this method, electron-ion interactions are evaluated using a semilocal, norm-conserving pseudopotential;[11] electronic exchange and correlation energies are calculated within the local-density approximation (LDA);[12,13] and the temperature is assumed to be zero.

Because the three metallic structures are very close in energy, it is necessary to calculate total energy differences very accurately. To accomplish this, a large Fourier expansion cutoff energy (30 Ry) is used, and the irreducible part of the Brillouin zone is sampled at a large number (550) of points. These values were chosen to produce relative energies that are converged to within 0.05 mRy/atom. Typically, this degree of precision is not achievable when comparing different structures since systematic errors are usually larger. However, because the systems involved are so similar, errors tend to be correlated and therefore cancel in energy differences.

All structural parameters for the three phases are optimized at each unit cell volume, with the degree of op-

TABLE I. Comparison between calculated structural parameters for the β-Sn, *Imma*, and sh phases and reported measurements from Ref. 1.

Structure	Volume (a.u./atom)	Theory (present work)	Experiment (from Ref. 1)
sh	89	$c/a=0.534$	0.533
Imma	92	$c/a=0.537$	0.538
		$b/a=0.950$	0.950
		$u=0.185$	0.193
β-Sn	95	$c/a=0.549$	0.551

timization governed by the desired precision in relative energies. Energy minimization is carried out for a given structure and volume by stepping along the gradient of the energy with respect to structural parameters until the magnitude of the gradient is smaller than a specified threshold. The gradient of the total energy with respect to structural parameters is calculated using *ab initio* determined quantum-mechanical forces[8] and stresses.[14]

The calculated volume dependence of the optimal structural parameters of the three phases is presented in Fig. 2. Points with dashed lines through them represent parameters that are constant by definition. Errors in the parameter values are comparable to or smaller than the size of the dots that denote the data points. The computed structural parameters are in excellent agreement with reported experimental values of Ref. 1 as is shown in Table I.

At large volumes, the optimal *Imma* structure is close to β-Sn structure. However as this phase is compressed, its structural parameters are found to diverge from the β-Sn values and approach the sh values. By a volume of 86 a.u./atom, the sh and *Imma* structures are nearly indistinguishable, whereas for intermediate volumes all three structures are clearly distinct. The rate at which
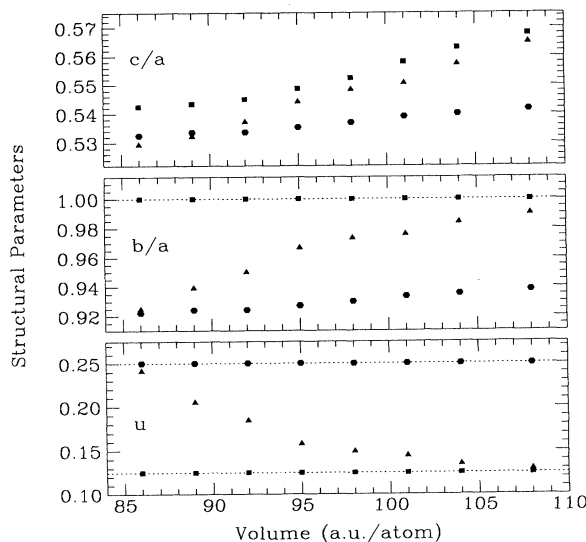

FIG. 2. Calculated volume dependence of the optimal structural parameters of the *Imma* (triangles), β-Sn (squares), and sh (hexagons) structures. Points with dashed lines through them represent parameters that are constant by definition. Errors in the parameter values are comparable to or smaller than the size of the dots.

the *Imma* phase changes with volume can also be seen in Fig. 2. As it is compressed, the *Imma* phase deviates slowly from β-Sn structure, but by 95 a.u./atom it starts rapidly changing into the sh structure.

Calculated equations of state for the three phases of Si are shown in Fig. 3, where solid lines are fits of computed data points (solid dots) for each structure to the Birch equation of state.[15] The fits for the β-Sn and sh structures are in good agreement with previous calculations.[2,6,7]

The total energy for the optimal *Imma* structure is calculated to be lower than that of β-Sn structure for all volumes considered. However, at large volumes (low and negative pressures) where the two structures are quite similar, the difference in energies of the two phases is within the systematic uncertainty of the calculation. At relatively low pressures experiments observe only the β-Sn phase even though the calculations show that the *Imma* structure is competitive if not lower in energy than the β-Sn structure. Since the two structures are so similar in this pressure region, perhaps they are indiscernable at finite temperatures, which could explain the discrepancy between theory and experiment.

The *Imma* phase is also found to be lower in energy than the sh phase for all but the smallest volumes, where the two equations of state merge. It is interesting to note that the merging of the total energies (at $\sim$90 a.u./atom) occurs while the two structures are still distinct (see Fig. 2). This point is discussed below.

Transformation of the *Imma* phase from the β-Sn-like to the sh-like structure results from relative changes in the various terms of the total energy as a function of cell volume. The total energy can be viewed as the sum of five terms:

$$E_{\text{tot}} = E_{1-\text{el}} + E_{\text{Hartree}} + E_{xc} + E_{\text{Ewald}} + E_\alpha, \qquad (1)$$

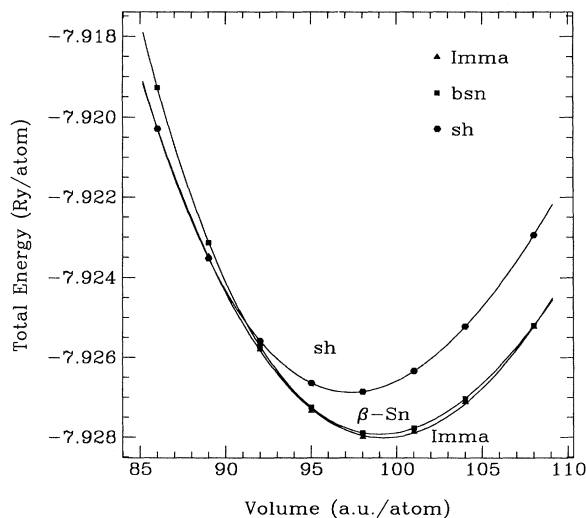where $E_{1-\text{el}}$ (also called the band energy) is associated

with single-electron effects such as kinetic energy and the electron-ion interaction; E_{Hartree} is the direct electron-electron Coulomb energy (Hartree energy); E_{xc} is the sum of the exchange and correlation energies; E_{Ewald} is the ion-ion Coulomb energy (Ewald energy); and E_α is a term to account for the difference between the pseudopotential and a Coulomb potential. Figure 4 shows the volume dependences of the first four terms of Eq. (1) for the β-Sn and sh phases relative to the *Imma* phase. The E_α term is essentially the same for all three phases.

Because electrons and ions are more uniformly distributed in the more closely packed sh structure, the repulsive Coulomb-based terms, E_{Hartree} and E_{Ewald}, tend to favor this phase over the β-Sn structure. Conversely, the band and exchange and correlation energies tend to favor the β-Sn structure. For $E_{1-\text{el}}$ this trend is due to greater band dispersion in the more highly coordinated sh phase; whereas for E_{xc} the trend is due to the attractive nature of the exchange interaction which favors less uniform electron distributions.

At large volumes the band and exchange and correlation terms dominate the relative total energies, so that the lowest energy structure is β-Sn-like. However, as volume decreases the repulsive Coulomb-based terms become more dominant, and the lowest energy structure becomes more sh-like. It is interesting to note that the *Imma* structure is not favored by any individual term of the total energy, but that the terms cancel in such a way as to make it lowest in energy. Figure 4 also explains the merging of the *Imma* and sh equations of state while the structures are still different (see above). Individual total-energy components for the two phases remain distinct as long as the structures do. However the terms combine to produce comparable total energies even before the structures have merged.
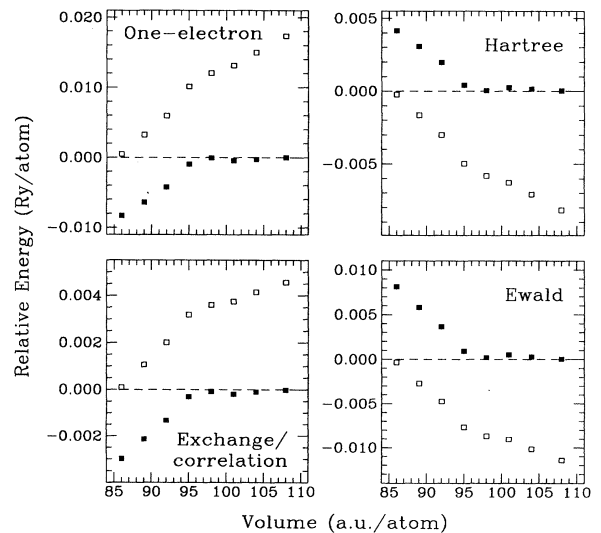

FIG. 3. Calculated total energy vs volume, fitted to the Birch equation of state (Ref. 15), for Si in the *Imma*, β-Sn, and sh structures.

FIG. 4. Volume dependence of the one-electron, Hartree, exchange and correlation, and Ewald terms of the total energy for Si in the β-Sn (filled squares) and sh (open squares) structures. Energies are measured relative to the values for the *Imma* structure at each volume, so that the dashed line through zero on each panel corresponds to the *Imma* phase.

The authors of Ref. 1 speculate that a transition from the β-Sn to the *Imma* structure might account for the discontinuous jump observed in the superconducting transition temperature (T_c) in the same pressure region.[16] However, the present calculation of a continuous *Imma*-based transformation to the sh structure would seem to contradict this hypothesis. A calculation of electron-lattice coupling and T_c of Si in the *Imma* structure is beyond the scope of this study, however two possible explanations of the discontinuity observed in T_c are offered. One possiblity is tied to an increase in the rate of change of the *Imma* structure for volumes $\lesssim 95$ a.u./atom (see above). If this effect were to manifest itself in analogous changes in the phonon frequencies or density of states at the Fermi level, then a shift in T_c that appears discontinuous might occur. We have calculated the volume dependence of the density of states at the Fermi level and have found no rapid change near 95 a.u./atom. Another explanation is the possibility of slight pressure inhomogeneities in the T_c versus pressure measurements causing discontinuous structural transformations.

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