Prediction of a metastable phase of silicon in the Ibam structure

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Prediction of a new metastable phase of silicon in the *Ibam* structure

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In a study aimed at finding new useful forms of silicon, we use an *ab initio* random structure searching (AIRSS) method to identify a new phase of silicon in the *Ibam* structure. The *Ibam* phase is found to be semimetallic within density functional theory with a small band overlap, and it is expected that quasiparticle corrections using the GW approximation would yield a semiconducting state with a small band gap. Calculation of the lattice dynamics reveals that the structure is locally stable. Enthalpy-pressure relations are calculated for the *Ibam* structure as well as all other known Si structures, including the previously predicted phases st12 and bct. These results indicate that *Ibam* silicon is metastable over the pressure range considered. Calculated coexistence pressures of the other known phase transitions are in good agreement with experimental observation.

The high-pressure phase diagram of silicon has been the focus of numerous experimental and theoretical studies because of its extreme technological importance. A major goal is to find new structural phases with desirable electronic properties such as direct band gaps and useful optical spectra for applications. High-pressure phases of Si have have been studied experimentally up to at least 248 GPa[1] and the observed phase transitions have in general been in good agreement with theoretical predictions[2–11]. It is also known that upon slow pressure release from the metallic β-Sn phase that Si does not return to the cubic diamond phase but instead transforms into a number of metastable phases with distorted tetrahedral bonding, namely the r8 and bc8 phases of Si[11,12]. However, other phases have been reportedly obtained with different conditions of pressure release. Upon rapid release of pressure (<100 ms) two other phases of silicon were obtained, referred to as Si-VIII and Si-IX, however only incomplete structural information could be obtained from the x-ray diffraction pattern[13] and hence electronic structure calculations are not possible. Furthermore, nanoindentation experiments in silicon have resulted in the observation of another phase, Si-XIII, although little is known regarding its structure[14,15].

The lack of information about the low-pressure phase diagram of Si is unfortunate because while cubic silicon has many characteristics which make it favorable for modern technological applications, it should be possible to improve on some of these by using a closely related silicon polytype. Because it is possible that one of the phases previously obtained but unidentified may have desirable electronic, optical, or other properties that would be an improvement on existing silicon technology based on cubic silicon, several unidentified phases are being studied. This idea is behind recent theoretical studies of the optical spectra in both known metastable phases of Si as well as doped cubic silicon in the hope of obtaining better absorption characteristics relevant to photovoltaic devices[16–18].

In this Letter we use *ab initio* random structure searching (AIRSS)[19] to further explore the phase diagram of Si. In particular we target the phase Si-IX, which is one of the two phases obtained from rapid depressurization from 12 GPa in diamond anvil cell experiments[13]. The experimental x-ray diffraction lines could be indexed on the basis of a tetragonal unit cell with cell parameters a =7.482 Å and c =3.856 Å. By assuming the same density as nearby metastable phases it was estimated that the unit cell contains 12 atoms, although the atomic positions were undetermined. It was noted that this phase is not equivalent to the known, metastable silicon phase st12.

We conduct our structure search by randomly generating 5000 structures with 12 atoms in the unit cell with the experimentally determined cell parameters. The atomic positions are then optimized to their lowest energy configuration using the local density approximation (LDA) to density functional theory (DFT) as implemented in VASP using the projector augmented wave method[20–22]. We employ a planewave cutoff energy of 350 eV and a Monkhorst-Pack Brillouin zone sampling grid with a resolution of $2\pi\times0.04$ Å^{-1}. In order to evaluate the dynamical stability of the resulting structures we calculate phonon frequencies throughout the Brillouin zone using density-functional perturbation theory (DFPT) as implemented in the Quantum-ESPRESSO package[23]. Thermodynamic stability and the equation of states for the various polytypes of Si are also computed within Quantum-ESPRESSO using the planewave pseudopotential method[24,25] with norm-conserving pseudopotentials and a kinetic energy cutoff of 40 Ry.

The random structure search results in a single lowest energy structure[26]. Symmetry analysis reveals that the structure corresponds to the orthorhombic space group *Ibam* with atoms in the 8(j) and 4(a) Wyckoff positions. However, calculation of the stress tensor for this structure reveals that there is a slight nonuniform pressure which distorts the cell parameters from a tetragonal to an orthorhombic cell. The fully relaxed structure at 0 GPa retains the *Ibam* symmetry with a =3.872 Å, b =7.887 Å, and c =6.877 Å. The atomic positions are located at the 8(j) sites with x=0.25201 and y=0.16322 and the 4(a)

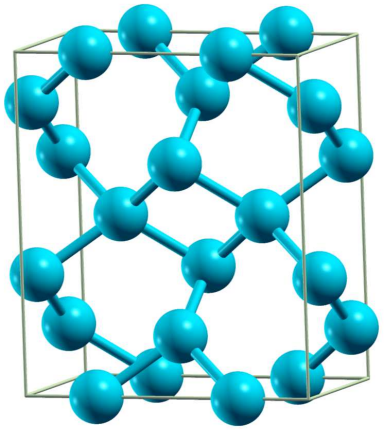

FIG. 1. (Color online) Structure of *Ibam* Si.

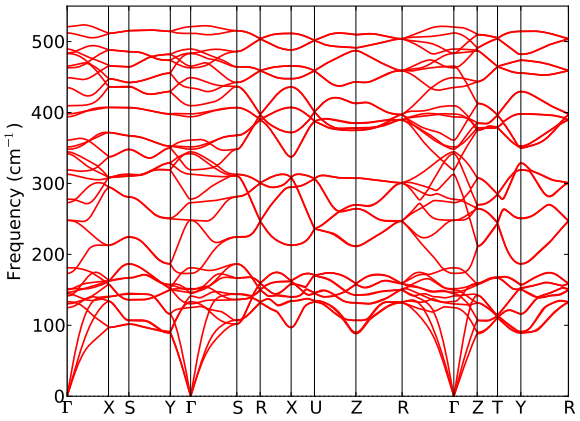

FIG. 2. (Color online) Phonon dispersion of *Ibam* Si plotted along the high-symmetry lines of the Brillouin zone

sites with z=0.25. This structure, shown in Fig. 1, has distorted tetrahedral bonding with the interesting feature of having four-fold rings. These four-fold rings are connected in a chain-like manner, similar to that found in SiS_2 and $SiSe_2$ which also take the *Ibam* structure[27]. The presence of only even-membered rings opens up the possibility of this structure forming in III-V semiconductors because of the absence of energetically unfavorable same-species bonds.

The bond lengths in the *Ibam* structure are similar to those found in the cubic phase of silicon. Around the 4(a) sites there is a single bond length of 2.359 Å, with three distinct angles of 86.4°, 113.9°, and 131.1°. The 8(j) sites have two distinct bond lengths of 2.359 Å bridging to the 4(a) sites and 2.371 Å between neighboring 8(j) sites. Around the 8(j) sites there are four distinct bond angles of 93.6°, 130.7°, 109.5°, and 88.7°. As already mentioned, the fully relaxed *Ibam* structure is similar although not identical to the structural parameters experimentally determined by Zhao *et al.*[13]. Relaxation of the cell stress alters the lattice constants by 0.4%, 5.4%, and -8.0%, although there is no change in the symmetry type or nature of the bonding. Simulations of the x-ray diffraction spectra for both the structure with a fixed cell and a relaxed cell show some agreement with the diffraction peaks found in experiment, however the agreement is insufficient to unambiguously identify Si-IX as being in the *Ibam* structure. Phonon frequencies are also calculated for the *Ibam* structure on a 6×3×3 grid of q-vectors in the Brillouin zone and all frequencies were found to be real, indicating that the structure is locally stable. The resulting phonon dispersion plotted throughout the Brillouin zone is shown in Fig. 2.

The bandstructure of *Ibam* Si is shown in Fig. 3 plotted throughout the orthorhombic Brillouin zone. *Ibam* Si is predicted within the LDA to be semimetallic as can be seen in Fig. 3 and from the small but finite density of states present at the Fermi level in Fig. 4. There is a slight direct overlap at Γ of approximately 0.275 eV, although the (occupied) band minimum of the would-be conduction manifold is located off the high-symmetry lines at the point P=(0.4,0,0.35) in reciprocal coordinates. This band minimum is located 0.35 eV below what would be the valence band maximum at Γ in the case of a band gap opening. Calculations based on LDA-DFT approaches are known to inadequately predict quasiparticle energies. However, generally agreement with experiment can be obtained by including quasiparticle self-energy corrections as calculated within the GW approximation[28]. Although such calculations are beyond the scope of the present study, these corrections are of sufficient magnitude in other phases of Si[29] that it is expected that *Ibam* Si would become semiconducting. It is also worth noting that the Si-IX structure obtained by Zhao *et al.* was believed to be either semimetallic or a narrow-band semiconductor[13]. Finally, the sudden large increase in the density of states near the Fermi level as shown in Fig. 4 and the many-valley nature of the bandstructure as seen in Fig. 3 suggests that *Ibam* Si be could be of interest as a superconductor if it were doped. Many-valley phonon scattering processes can give rise to superconductivity as a result of the large number of states available for scattering in addition to the fact that intervalley processes involve large momentum transfers and thus tend to be screened less than intravalley processes[30].

In order to evaluate the thermodynamic stability of the *Ibam* phase, we have performed total energy calculations on all experimentally observed silicon phases and have also included the predicted metastable phases st12 and the recently predicted bct phase[31]. For each phase, total energies are calculated while fully relaxing the cell under a fixed volume, and the resulting E(V) data is fit with a Birch-Murnaghan equation of state[32]. The resulting fits are shown in Fig 5. Pressure-volume curves were obtained by numerical differentiation of the total-energy curves (as shown in Fig. 6) and were used to produce the

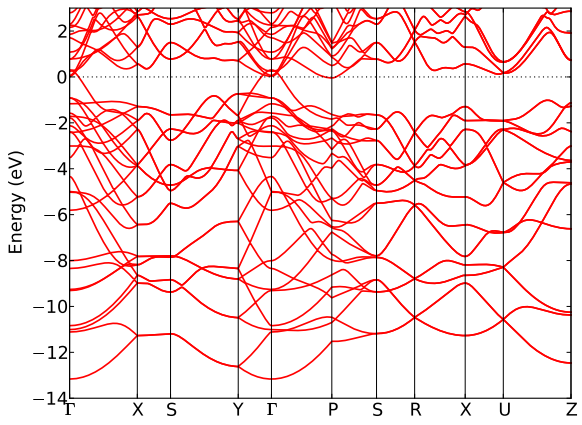

FIG. 3. (Color online) Bandstructure of *Ibam* Si. The Fermi level is at zero energy.

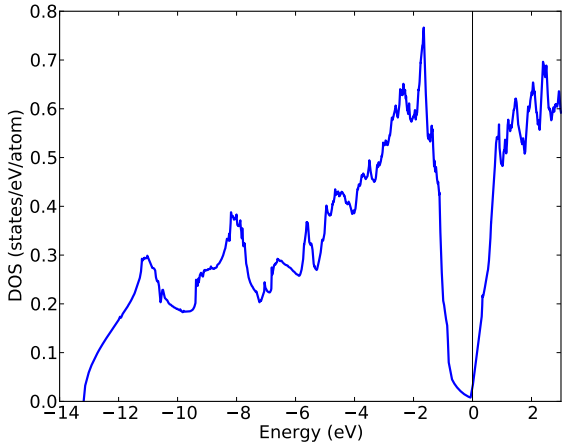

FIG. 4. (Color online) Electronic density of states (DOS) of Si in the *Ibam* structure. The Fermi level is at zero energy.

enthalpy versus pressure curves shown in Fig. 7.

For the range of pressures studied, the *Ibam* phase of silicon is never the lowest enthalpy structure and so is always a metastable phase. This does not preclude the possible observation of the *Ibam* structure however, as the conditions present in experiment and the activation barriers between phases play an important role. Although the r8 and bc8 phases also have higher enthalpy than cubic silicon for all pressures, they are present in experiments resulting from decompression from the β-Sn phase. There is also the possibility that germanium could form in the *Ibam* structure because of the similar, but not identical, correspondence between the phase diagram of Si and Ge. For example, the bc8 and r8 phases are favored over st12 in Si, but in Ge the reverse is true and st12 is obtained at zero pressure.

From our calculations we can also compare the calculated coexistence pressures for the other known phase transitions in Si. The cubic silicon to β-Sn transition occurs within a pressure range of 8.8-12.5 GPa[7]. Our calculations predict this transition to occur at a pressure of 9.2 GPa in good agreement with the experimental data and in better agreement than previous theoretical results which lie between 7.8-8.8 GPa[7]. Experimentally, upon increasing the pressure from β-Sn, Si takes on the *Imma* structure at 13.2 GPa[5]. Our calculations predict that the cubic phase transforms to *Imma* at a pressure of 9.1 GPa, lower than that of β-Sn transition. This result is in agreement with the results of Lewis and Cohen[4] who find the total energy of the *Imma* structure to be lower than that of β-Sn for all volumes considered in their calculation. The *Imma* and β-Sn structures are very similar in this pressure region and have nearly degenerate enthalpy curves. It has been argued that this similarity might make them experimentally indistinguishable at finite temperatures which leads to the discrepancy between theory and experiment[4].

The *Imma* structure is found to transform to the simple-hexagonal (sh) structure at 15.4 GPa by McMahon *et al.*[5], although other theoretical calculations have shown that the *Imma* phase is lower in energy than sh for all but the smallest volumes[4]. Our calculations predict a transition from *Imma* $\rightarrow$ sh at a pressure of 30.5 GPa, although this value is extremely sensitive because of the merging of the *Imma* and sh curves at low volumes and high pressures. The sh phase is observed to transform to the *Cmca* phase at a pressure of 38 GPa[9]. We find a transition pressure of 41.4 GPa, which is in somewhat better agreement that of 33 GPa found in previous calculations[10]. From the *Cmca* phase silicon is found experimentally to transform to the hexagonal close-packed (hcp) phase at 42 GPa[9]. Our calculations predict a transition at 50.6 GPa, which is in slightly larger disagreement with the experimental measurement than a previous calculation by Christensen *et al.* of 41 GPa[10]. Finally, the hcp phase is found to transform at $\sim$80 GPa to fcc and remains in this structure up to the highest pressure explored of 248 GPa[1]. Our calculations predict a transition pressure of 87.5 GPa, which is both in good agreement with experiment and with the previous value of 84.3 GPa calculated by Needs and Mujica[7].

Our calculations also allow us to determine the transition pressures obtained upon decompression from the β-Sn phase. We find a transition from β-Sn to the r8 phase at 8.4 GPa, which compares well with the experimental transition at 9.4 GPa[8] and previous calculations from Pfrommer *et al.* of 7.4 GPa[12]. We also calculate the transition from r8 to bc8 to occur at 1.8 GPa, in excellent agreement with experiment (2 GPa)[6] and prior theoretical calculations (1.9 GPa)[12].

An interesting new prediction from our enthalpy calculations is the fact that the previously predicted bct phase of Si[31] is found to have a lower enthalpy than the bc8 phase at 0.65 GPa. This phase was recently discovered in molecular dynamics simulations on carbon[33] and

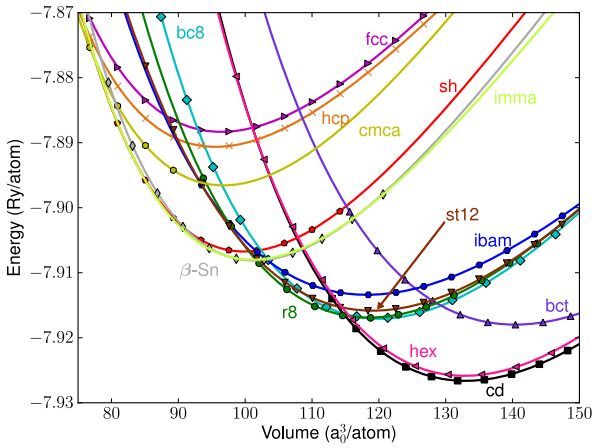

FIG. 5. (Color online) Comparison of the energy-volume curves for observed and predicted phases of silicon. The markers correspond to calculated data points and the lines are fits to the equation of state.

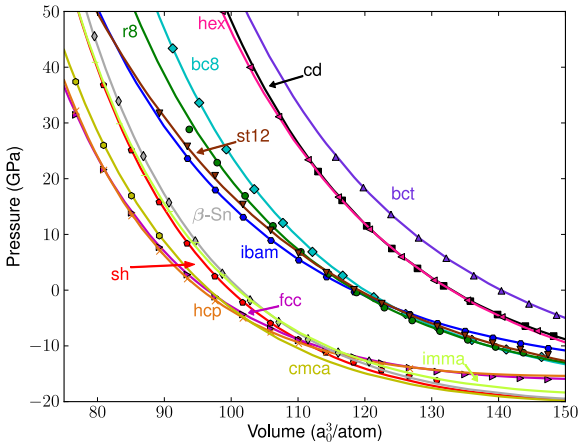

FIG. 6. (Color online) Pressure-volume curves for observed and predicted phases of silicon. The markers correspond to data points and the curves are obtained from numerical differentiation from the E(V) equation of state.

subsequent calculations predicted its existence in Si[31]. Calculations by Fujimoto *et al.*[31] had compared the bct phase with cubic Si and predicted that cubic Si would transform to the bct structure at -11.2 GPa. This is in good agreement with our calculations suggesting the value of -13 GPa. While, to our knowledge, experiments have not obtained bct Si at ambient conditions upon depressurization, the positive coexistence pressure of 0.65 GPa indicates that bct Si may be easier to obtain than previous calculations have suggested.

In summary, we predict a new phase of silicon in the *Ibam* structure using *ab initio* random structure searching. This phase may be accessible experimentally in samples of Si decompressed from the β-Sn phase. Calculations of the electronic structure reveal that it is semimetallic within LDA with a small band overlap of 0.35 eV. It is expected that quasiparticle corrections using the GW approximation would open up the gap and result in a semiconductor. Calculations regarding energetic stability suggest that this phase is metastable over the pressure range studied. In addition, our calculated transition pressures for other known phases of silicon are in good agreement with experimental observation, often improving on previous theoretical results. We also find that the bct phase of Si recently predicted by Fujimoto *et al.*[31] has a calculated coexistence pressure of 0.65 GPa with the bc8 phase of Si, which is known to exist at ambient conditions upon depressurization from the β-Sn phase.

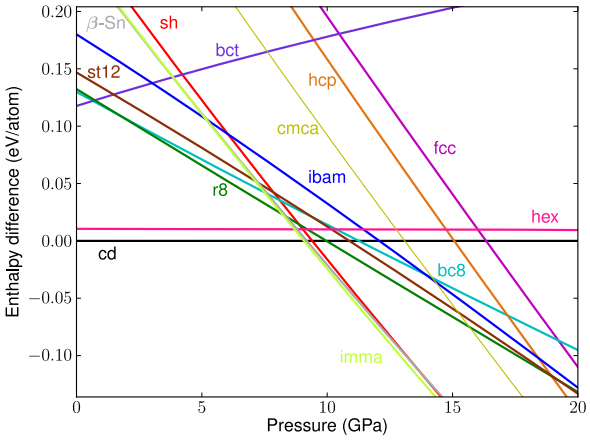

FIG. 7. (Color online) Enthalpy-pressure curves for observed and predicted phases of silicon. The enthalpy differences are taken relative to silicon in the cubic diamond phase.

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