

Structural and electronic properties of the high-pressure hexagonal phases of Si

K. J. Chang and Marvin L. Cohen

Department of Physics, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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The pseudopotential method is used to examine the structural transitions of Si from β -Sn to simple hexagonal to hexagonal close packed. The calculated transition pressures, transition volumes, and c/a ratios are in good agreement with the measured values. For the simple hexagonal phase, a soft-phonon mode and a high density of states at the Fermi level are found. These properties and the strong covalent interlayer bonding suggest the existence of superconductivity in this system. Investigation of the band structure reveals parallel bands separated by about 3 eV along the LH axis of the Brillouin zone; these are the likely origin of the main peak in the optical spectrum.

There have been two recent reports^{1,2} of a transformation of Si from the β -Sn to the simple hexagonal (sh) structure at pressures of 160 (Ref. 1) and 130 (Ref. 2) kbar. These represent the first observations of a monatomic system in the sh phase.³ This structural transformation and another¹ to the hexagonal-closed-packed (hcp) structure at 400 kbar can be viewed in terms of simple displacements of atoms, followed by a slight modification of the interatomic distances (see Fig. 1).

In this work we present pseudopotential calculations of the structural stability of β -Sn, sh, and hcp Si, and of the electronic properties for the sh phase. The calculations indicate that the phase-transition sequence of β -Sn \rightarrow sh \rightarrow hcp results from a pressure-sensitive soft-phonon mode associated with intralayer forces. For the sh phase there is strong interlayer covalentlike bonding yielding a system opposite to the graphite case which is covalent in the layers with weak Van der Waals bonding between layers.⁴ The calculated density of states at the Fermi level is high, suggesting that superconductivity is likely in this Si phase at temperatures comparable that of β -Sn.⁵ A detailed band-structure calculation yields almost parallel bands separated by a ~ 3 -eV gap along the LH direction in the Brillouin zone. This structure should contribute to a peak in the joint density of states and in the optical constants.

The calculations are based on the pseudopotential total energy scheme⁶ within the local density-functional theory,⁷ using the Wigner interpolation formula⁸ for the exchange

and correlation functional. The *ab initio* pseudopotentials⁹ used here were successfully employed in previous calculation of Si.¹⁰ A plane-wave basis set with a kinetic energy cutoff up to 11.5 Ry is used. A grid of 10 special k points in the irreducible Brillouin zone is chosen for diamond, 75 for β -Sn and hcp, and 150 for sh. The resulting convergence is better than 1 mRy/atom. The total energies for each phase, β -Sn, sh, and hcp, are optimized by variations of c/a and fitted to the Murnaghan's equation of state.¹¹

Figure 2 shows the total structural energies as a function of volume. The computed transition pressure of 93 kbar from diamond to β -Sn is consistent with one previously calculated result¹⁰ and higher than another calculated value of 70 kbar.¹² There is a range of measured values^{1,2,13} from 88 to 125 kbar. Analysis of these data suggests that 110 kbar could be considered as an appropriate value.¹⁴

The calculated transition pressure to the sh phase is 120 kbar. The measured values are 130 (Ref. 2) and 160 (Ref. 1) kbar. For this case, we consider this reasonably good agreement since the calculated pressure is very sensitive to the number of k points used because of the proximity of the total energy curves (Fig. 2) between the β -Sn and sh phases and the finite grids used to represent the band overlap in k

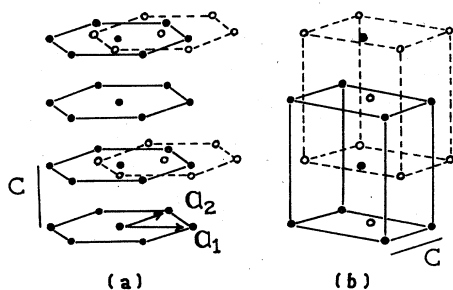


FIG. 1. Structural relationships between (a) sh and hcp, and between (b) sh and β -Sn. The orthorhombic structure in (b) is obtained from sh in (a). The open dots denote transformed atoms.

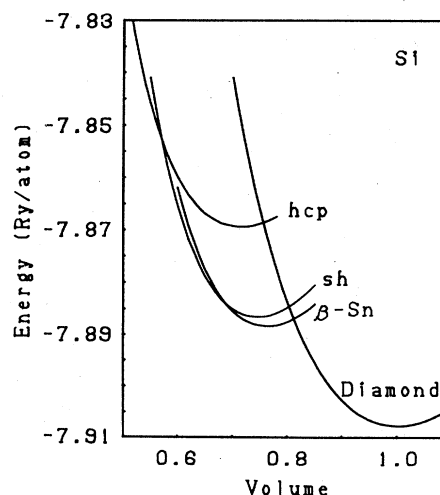


FIG. 2. Total structural energy vs the volume normalized by the calculated equilibrium volume in diamond.

space. With 40 k points for β -Sn and 75 for sh, the pressure increases by 70 kbar. The sh phase is calculated to transform into the hcp structure at 410 kbar. The hcp phase is found to be stable at 400 kbar,¹ and this pressure is close to the calculated value.

We have found that the transition volumes,¹⁵ 0.707 (β -Sn) and 0.692 (sh) for the β -Sn to sh and 0.603 (sh) and 0.556 (hcp) for sh to hcp transformations, are in good agreement with the measured values in Refs. 1 and 2. The c/a ratios are estimated to be 0.551 for β -Sn at a volume of 16 $\text{\AA}^3/\text{atom}$, 0.955 for sh at 13.5 $\text{\AA}^3/\text{atom}$, and 1.695 for hcp at 11.1 $\text{\AA}^3/\text{atom}$. The agreement with the experimental values of 0.552 (β -Sn), 0.94 (sh), and 1.698 (hcp) is also excellent.

Both the hcp and the β -Sn structures can be formed from the sh phase. Figure 1 shows the hcp structure determined by a displacement of $(\bar{a}_1 + \bar{a}_2)/3$ of one basal plane, accompanied by a modification of the c/a ratio. This displacement corresponds to a transverse acoustic (TA) phonon mode at the A point in the Brillouin zone. Our calculated phonon frequencies are 13.5 THz at a volume of 12.6 $\text{\AA}^3/\text{atom}$ for the longitudinal (LA) mode, and a very soft TA frequency of 3.5 THz. As the volume is compressed the TA modes becomes softer, whereas the LA frequency increases. The soft transverse mode is caused by the relatively weak bonding in the layer which is also connected with the sh-hcp transition. This will be discussed later.

We find that the structural energy barrier at the intermediate state between sh and hcp decreases as the volume is reduced. At a volume close to the hcp transition volume, we find no restoring forces, and thus the transverse distortions destabilize the sh structure. This results from the negative pressure dependence of the TA mode. Furthermore, this energy barrier is noted to be effectively reduced by a slight change of c/a required in bringing the sh phase into the hcp structure for each intermediate transverse displacement. As shown in Fig. 1, the β -Sn structure is also produced from sh by displacing one of the interpenetrating body-centered orthorhombic sublattices in the direction of the a axis by $a/4$, followed by a slight change of the c/a ratio. Hence, the a axis of sh becomes the c axis of β -Sn. Since this displacement is transverse to the interlayer axis, it does not cost much energy to transform sh into β -Sn. This movement is also equivalent to the soft optic mode in β -Sn.¹² In fact, the c axis of sh is slightly enlarged when Si transforms from β -Sn to sh. This relaxation stabilizes the sh structure since the LA mode in sh is very strong.

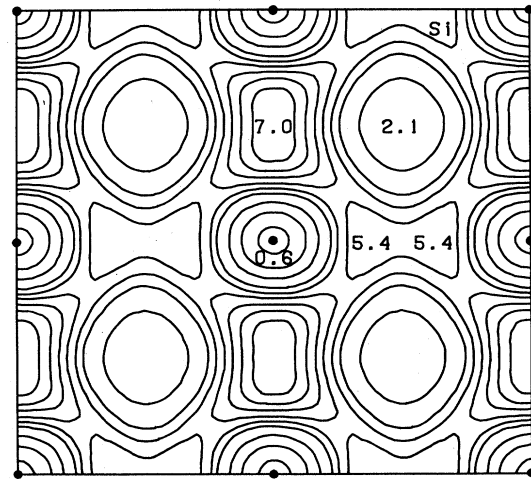


FIG. 3. Charge density contour plot in the $[10\bar{1}0]$ plane for the sh phase at a volume of 12.6 $\text{\AA}^3/\text{atom}$ in units of electrons per cell volume.

As shown in Fig. 3, the sh phase has a large pileup of covalent charge along the c axis while the charge density along the a axis has a local minimum in the middle of the bond. This character is entirely different from the weak bonding existing between layers in the graphite structure.⁴ Hence, the distortion along the interlayer axis produces a stronger restoring force than in the plane. The ratio of the peak charge density to that of the empty region is also larger than that of a normal metal. The linear chainlike bonding along the c -axis resembles that of an A15 compound and thus might produce a strong electron-phonon interaction and superconductivity. In addition, the density of states¹⁶ (DOS) of 4.4 (electrons/atom)/Ry at the Fermi level $N(E_F)$ is found to be comparable to that of simple metals.

The detailed band structure and DOS is shown in Fig. 4. The DOS has peaks on both sides of E_F . An angular momentum decomposition of the DOS indicates that the lower peak is mostly p -like whereas the upper peak consists of p - and d -like contributions. The d -like DOS in the upper peak is found to arise mainly from a local minimum of the lowest unoccupied state with the d and s electrons at L . Along the LH axis the lowest two states are decomposed into p -like contributions. Furthermore, the first conduction and the second valence states along LH are almost parallel

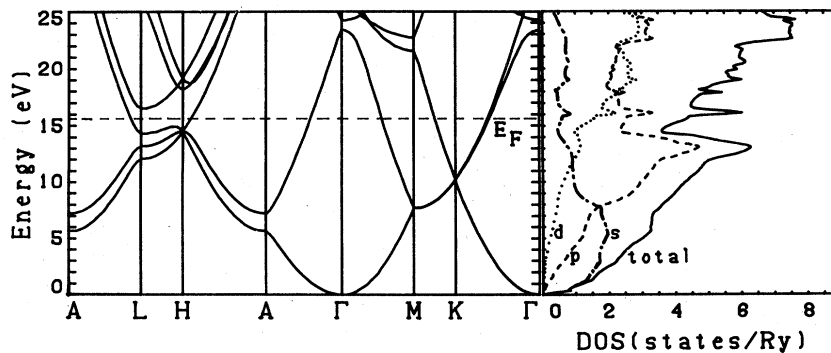


FIG. 4. Band structure, DOS, and angular momentum decomposition of the DOS for the sh phase at a volume of 12.6 $\text{\AA}^3/\text{atom}$.

and separated by about 3 eV. As the pressure increases, these bands move toward the Fermi level, and thus the separation decreases. Using optical selection rules, strong interband transitions are expected along LH between these two bands. A reflection spectrum¹⁷ around 200 kbar shows a pronounced absorption band near 2.5 eV and we tentatively associate this absorption with these transitions.

In conclusion, we have calculated structural and electronic properties of high-pressure Si phases, and we have shown that successive phase transformations of $\beta\text{-Sn} \rightarrow \text{sh} \rightarrow \text{hcp}$ can be interpreted in terms of a soft-transverse-phonon mode. The sh phase of Si under pressure has been found to have a high DOS at the Fermi level and strong covalent-like bonding in the interlayer direction. Although more detailed analyses of the electron-phonon matrix elements are

necessary to predict superconductivity, the present results for the electronic and bonding structures suggest that Si in the sh phase might be a good superconductor.

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