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Theoretical high-pressure studies of silicon VI

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We have investigated Si theoretically under high compressions by means of first-principles self-consistent total-energy calculations within the local-density approximation using the full-potential linear-muffin-tin-orbital method. Our results confirm the recent high-pressure experimental observations of crystallographic phase transformations in Si [Hanfland *et al.*, Phys. Rev. Lett. **82**, 1197 (1999)]. The calculated transition pressure for the occurrence of the silicon-VI crystal structure agrees very well with the experimental data. [S0163-1829(99)01045-0]

The high-pressure phase diagrams of the group-IV elements, and in particular Si, have attracted a lot of attention, both experimentally and theoretically. At ambient conditions, Si is stable in the diamond-type structure.[1] Jamieson[2] has shown that it transforms to the β-Sn structure around 12 GPa. The β-Sn structure is stable up to 16 GPa, where it transforms to the primitive hexagonal (ph) structure.[3–6] Recently, Nelmes and co-workers[7,8] have shown that there is an intermediate phase between the β-Sn structure and the primitive hexagonal structure in the pressure range of 13–16 GPa. The structure of this new phase is orthorhombic with the $Imma$ space group. It is also shown that Si becomes a superconductor in its high-pressure, primitive hexagonal phase.[9] The primitive hexagonal phase transforms to the hexagonal close packed (hcp) phase at 42 GPa and this hcp phase transforms to the fcc phase at 78 GPa.[6,10] However, also a new phase (Si-VI) appears around 40 GPa but the structure of this phase has been unknown until just recently. Earlier the structure of this phase was assumed to be double hexagonal close packed (dhcp). Very recently Hanfland *et al.*[11] performed most interesting high-pressure experiments for Si using high-resolution monochromatic synchrotron x-ray diffraction. Their main result is the observation of an orthorhombic high-pressure phase at 38 GPa. They identified this high-pressure phase as similar to the Cs-V structure,[12] with the $Cmca$ space group. The axial ratios and atomic coordinates are nearly identical for both Si and Cs in this phase. On the theoretical side, *ab initio* calculations are performed for the previously observed phases that confirm the experimental data available at that time. Cohen and co-workers[13–15,9,16,17] have made a number of calculations on the structural phase transitions in Si at high pressure using the pseudopotential method. Their calculations also showed good agreement with available experimental data at that time. Also, Needs and Martin[18] and recently Needs and Mujica[19] have made a first-principles pseudopotential study of structural phase transitions in Si. Their calculations show the following structural sequence of phase transitions with increasing pressure; diamond structure $\rightarrow\beta$-Sn$\rightarrow$ph$\rightarrow$hcp$\rightarrow$dhcp$\rightarrow$fcc. Up to now we are not aware of any *ab initio* calculation for the newly observed Si-VI structure.

The main aim of the present paper is to use the experimental findings of the Si-VI phase and confirm it theoretically. This will also constitute a most sensitive test of the accuracy of the theoretical description of the electronic structure of Si.

In order to study the electronic structure of Si we have used the full-potential linear muffin-tin-orbital (FPLMTO) method.[20] The calculations were based on the local-density approximation. We used the Hedin-Lundqvist[21] parametrization for the exchange and correlation potential. Basis functions, electron densities, and potentials were calculated without any geometrical approximation.[20] These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l_{max}=6$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fou-

TABLE I. Calculated and experimental transition pressure (GPa) and lattice constants (Å).

	Transition Pressure		Lattice constants	
	Expt.[a]	Calc.	Expt.[a]	Calc.
Sh→Si-VI	38.0	34.0	$a=8.024$, $b=4.796$, $c=4.776$	$a=8.13$, $b=4.87$, $c=4.77$
Si-VI→Hcp	42.5	41.5	$a=2.473$, $b=2.473$, $c=4.188$	$a=2.47$, $b=2.47$, $c=4.18$

[a] Hanfland *et al.* (Ref. 11.

rier series in the interstitial region. The muffin-tin sphere occupied approximately 50% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site and principal as well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions.[22,23] In the calculations reported here, we made use of pseudocore $2p$ and valence band $3s$, $3p$, and $3d$ basis functions with corresponding two sets of energy parameters, one appropriate for the semicore $2p$ states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well-converged basis.[20] For sampling the irreducible wedge of the Brillouin zone (BZ) we used a uniform mesh of k points[24] and in the final convergence 50, 68, and 50 k points in the irreducible Brillouin zone (IBZ) were used for ph, Si-VI, and hcp structures, respectively. In order to speed up the convergence we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRy.

In Fig. 1 we show the total-energy difference between pertinent crystallographic structures for Si as a function of volume. Here we compare the ph, Si-VI, and hcp structures, where the energy of the Si-VI structure is taken as the reference level. For simplicity we have not considered the three low-pressure phases that are already confirmed by earlier *ab initio* calculations. In the calculations (not shown), we find that the theoretical equilibrium volume is largest for the ph structure and smallest for the hcp structure. This finding is directly consistent with the fact that the packing is more open for the primitive hexagonal structure and more closed packed for the hcp structure.

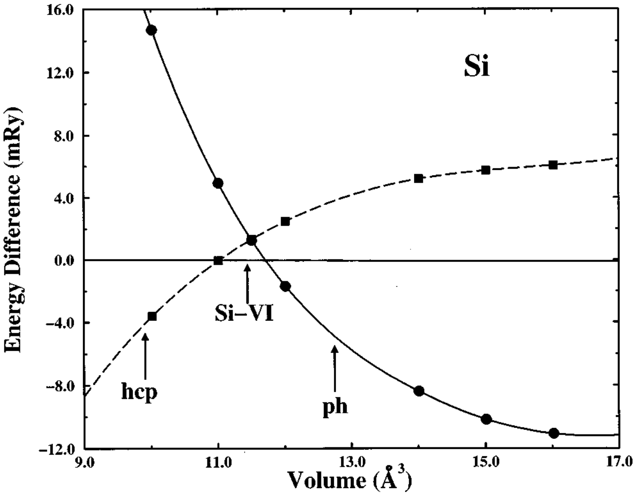

FIG. 1. Energy difference between the ph, hcp, and Si-VI crystal structures for Si as a function of volume. The Si-VI structure is used as the zero-energy reference level.

Under compression, the calculations show that Si undergoes a structural phase transition from ph to Si-VI. The calculated pressure for this transition is 34 GPa, which should be compared with the experimental value of 38 GPa.[11] After this crystallographic change the Si-VI phase is stable for a quite small range of volumes and when $V/V_0 \simeq 0.56$ the Si-VI phase is calculated to transform to the hcp phase. The theoretical pressure for this transition is 41.5 GPa to be compared with the experimental value of 42.5 GPa. The experimental volume of the hcp structure at the transition is $V/V_0 = 0.57$. The calculated and experimental transition pressures and lattice constants are also collected in Table I. The crystallographic behavior obtained from our full-potential calculations, shown in Fig. 1, is thus in very good agreement with experiment. It is also consistent with the above-mentioned, simple model for chemical bonding. As already mentioned, at the lowest volumes the structure with a better packing is stable, due to the dominance of the repulsive Born-Mayer energy.

In Table II we show our relaxed axial ratio and positional parameters for the Si-VI phase. Our calculated values are in excellent agreement with the experimental data. We have also compared our calculated c/a for the primitive hexagonal and hexagonal phase with the experimental c/a. This is shown in Table III and again the agreement between the experiment and theory is very good.

In order to understand the stability of the various structures, we have to consider the different contributions to the total energy. At high compression when the atoms are forced to have short distances between them, the valence electrons become more or less free-electron-like. In addition, the overlap repulsion between the valence states as well as the repulsion of low-lying core states (which at high compression have wave functions that start to overlap), give rise to a volume dependence of the total energy, which is similar to the classical Born-Mayer term.[25] Hence it may be useful to think about structural trends in this system as at least partly

TABLE II. Calculated and experimental lattice and internal parameters for the Si-VI phase. Calculated values are at $V/V_0=0.58$ and experimental values are at $V/V_0=0.57$, where $V_0=20$ Å^3.

	Calculated	Expt.[a]
$y(8f)$	0.176	0.173
$z(8f)$	0.330	0.328
$x(8d)$	0.216	0.218
a/b	1.670	1.673
c/b	0.980	0.996

[a] Hanfland *et al.* (Ref. 11).

TABLE III. Calculated and experimental c/a ratio for primitive hexagonal and hexagonal close packed phases.

	ph	hcp
Calculated and expt.[a]	0.950, 0.947 [a]	1.696, 1.698[a]

[a]Olijnyk *et al.* (Ref. 3).

being influenced by a Born-Meyer repulsion, that favors a high nearest-neighbor coordination number. The coordination number of Si in the different structures is 8 for the ph phase and 12 for the hcp structure. In the Si-VI structure, the coordination number is between 10 and 11. With increasing pressure Si thus shows an increase in the number of nearest-neighbor (nn); starting from 8 nn (ph), via a structure with 10–11 nn (Si-VI), into a phase with 12 nn (hcp). This is consistent with expectations from the repulsive terms of the total energy, although we point out that sometimes other terms in the total energy gives rise to unexpected findings, such as, for instance, the simple cubic phase in Ca.[26]

In summary we have shown that modern electronic structure theory is sufficiently developed to give an accurate description of the high-pressure behavior of the Si. Our calculations also confirm the recent experimental finding of a similar phase[12] in Cs (Cs-V) and Rb. These results will be published elsewhere.[27]

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