

Crystal data for high-pressure phases of silicon

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X-ray-diffraction data have been obtained on Si in a diamond anvil cell to pressures of ~ 50 GPa. Crystallographic data are presented in phase I (cubic, diamond), II (tetragonal, β -Sn), V (simple hexagonal), VII (hexagonal close-packed), and the metastable phase III [body-centered-cubic (BC8)] and on the coexistence of the phases. Comparison is made between these data and the predictions of *ab initio* calculations for these structures and their equations of state.

I. INTRODUCTION

There have been many studies of the high-pressure phases of Si since the pioneering work of Minomura and Drickamer.¹ These authors inferred a phase transition from a drop of several orders of magnitude in the resistivity. Since that time the transition has been studied using electrical resistance,²⁻⁷ x-ray diffraction (*in situ*⁸⁻¹² and on quenched specimens^{2,13}), and optical properties.¹⁴⁻¹⁶ Shock studies have also been carried out.¹⁷⁻¹⁹ These references are restricted to work on crystalline material and do not include extensive work in amorphous samples.

Early x-ray-diffraction studies^{6,8,9} reported only the cubic (diamond) to body-centered-tetragonal (β -Sn) transition, which occurs at ~ 11 GPa, and for which there have been several theoretical studies.²⁰⁻²⁸ More recent experiments¹⁰⁻¹² were partly motivated by the prediction²⁴ of a hexagonal-close-packed phase above 40 GPa, which has been observed by us¹² and other workers.¹⁰ However, an intermediate primitive hexagonal phase was also found^{10,11} on compression of the β -Sn phase above about 14 GPa. This phase has since been studied theoretically and confirmed to be a thermodynamically stable phase between ~ 14 and 43 GPa.^{27,28}

The labeling of the high-pressure phases is given in Table I and is consistent for the lower-pressure phases with Cannon's review of the phases of the elements.²⁹ Phase III is found on quenching the β -Sn phase at room temperature and is discussed in this paper. Since phase IV is assigned to a similar quenched phase to III,²⁹ the primitive hexagonal phase is designated V. The

hexagonal-close-packed phase is designated VII since Olijnyk *et al.*¹⁰ tentatively identified another high-pressure phase immediately before the hcp phase.

The observation of phases V and VII has been reported briefly by us in previous publications.^{11,12} The purpose of the present paper is to report further details of the principal transitions occurring at room temperatures on increase and decrease of pressure up to ~ 50 GPa for crystalline Si.

II. EXPERIMENTAL DETAILS

Experimental details of x-ray-diffraction procedures using both conventional and synchrotron sources have been discussed elsewhere.³⁰ In order to study the influence of nonhydrostatic stress on the transition, selected experiments were carried out with the sample compressed in the gasket without a fluid, and also with different compressing media, including one on Si compressed in solid argon, which should remain quasihydrostatic to ~ 50 GPa.³¹ The diamond cell was modified for this purpose, so that four screws could be located in the body of the cell, holding the piston back against the Belleville springs. Argon gas was fed to the sample area as the diamond cell was slowly cooled to 77 K. While still at 77 K, the four screws were retracted so that the springs pushed the piston forward, trapping solid argon in the sample cavity. Samples were in the form of lightly compacted disks of sufficiently small thickness that the diamond anvils could not compress them directly, as suggested by Werner *et al.*⁹

TABLE I. Designation of high-pressure phases stated in this paper (Refs. 29, 10, and 11).

Designation	Structure	Pressure region (GPa)
I	Cubic (diamond)	0 \rightarrow ~ 11
II	Body-centered tetragonal (β -Sn)	$\sim 11 \rightarrow 15$
III	Body-centered cubic ^a	$\sim 10 \rightarrow 0$
V	Primitive hexagonal	$\sim 14 \rightarrow 40$
VII	Hexagonal close-packed	~ 40

^aOften referred to as BC8 phase.

III. EXPERIMENTAL RESULTS

Experimental results will be discussed taking each phase and transition in turn.

A. Phase I (cubic, diamond)

The present experimental points are in good agreement with the x-ray-diffraction data of Senoo *et al.*³² to 8 GPa, but lie somewhat below the $V(P)$ curve of Vaidya and Kennedy³³ and significantly below the data of Bridgman, after revision of the data to account for changes in the pressure scale.³⁴ The discrepancy with the more modern piston-cylinder results of Vaidya and Kennedy is not understood. The best experimental values of the bulk modulus B_0 and its pressure derivative B'_0 at zero pressure are based on elastic constant data ($B_0=97.88$ GPa; $B'_0=4.24$).³⁵ The present data and those of Senoo *et al.*³² are consistent with the Murnaghan equation using these values, within experimental error.

Soma³⁶ calculated the $V(P)$ curve for Si(I) using a pseudopotential approach. The present experimental data lie just above the range of his calculated $V(P)$ values. A more recent calculation of Yin and Cohen²³ gives $B_0=98$ GPa, in excellent agreement with the present results.

B. I→II transition and phase II

Experimental results for the I→II transition and phase II are given in Table II. A strong case can be made for accepting these pressures (11.3–12.5 GPa onset and completion) as representative of hydrostatic conditions. Firstly, the samples were in the form of lightly compacted disks of thickness less than the minimum anvil separation so that anvil contact could not produce shear stresses in the samples. Secondly, essentially identical results were obtained using 4:1 methanol:ethanol solution, and solid argon. In both cases, ruby fluorescence peaks were well defined. Excellent agreement is noted for P_t with the optical experiment of Welber *et al.*¹⁴ using a 4:1 alcohol mixture.

The transition pressure is lowered by the application of nonhydrostatic stress. In one experiment, where the sample was held within a gasket, but without a pressurizing medium, a transition pressure onset of ~ 8.5 GPa was recorded. This is in good accord with the results of Gupta and Ruoff⁷ who found an initial drop in resistance at ~ 8 GPa when uniaxial stress was applied along the [111] direction.

Reasonable agreement for P_t and lattice parameters is obtained with Jamieson's early experiment⁸ within experimental error, but the present results are more precise. Olijnyk *et al.*¹⁰ also reported results on the I→II transi-

TABLE II. Comparison of experimental and theoretical data for phases I and II and the I→II transition.

Parameter	Present experiment	Other experiments	Theory
Cubic cell parameter a (Å) phase I, $P=0$		5.435 ^a	
Transition pressure P_t (GPa) I→II	Onset: 11.3±0.2 Completion: 12.5±0.2	See text	14.8, ^b 12.4–15.2, ^c 9.9, ^d 7.0, ^e 9.3 ^f
Lattice parameter a (Å) $P=P_t$, phase I	5.268±0.010 (at 11.3 GPa)	5.282 ^g (12 GPa)	5.214–5.226 ^c 5.301 ^d
$(V/V_0)(P_t)$, phase I	Onset: 0.911±0.003 Completion: 0.906±0.003	0.918 ^g at 12 GPa	0.883–0.889 ^c 0.928 ^d
Lattice parameters a, c (Å) phase II ($P=P_t$)	$a=4.69±0.006$ $c=2.578±0.005$		$a=4.705–4.720$, $c=2.499–2.502$ ^d $a=4.691$, $c=2.463$ ^e $a=4.715$, $c=2.593$ ^e $a=4.565$, $c=2.515$ ^f
c/a ratio	0.550±0.002	0.554 ^g	0.530, ^c (0.55±0.027) ^d 0.525, ^e 0.551 ^f
$(V/V_0)^{II}(P_t)$	0.706±0.003	0.709 ^g	0.696–0.700, ^c 0.718 ^d 0.707, ^e 0.707 ^d
$(V^I - V^{II})(P_t)$ $V^I(P_t)$	0.204±0.004	0.209 ^g	0.213–0.217, ^c 0.26 ^d

^aReference 29.

^bReference 20.

^cReference 21.

^dReference 23.

^eReference 27.

^fReference 28.

^gReference 8.

TABLE III. Experimental parameters for phase V and II→V transitions and comparison with theory.

Parameter	Present experiment	Olijnyk <i>et al.</i> ^a experiment	Theory
Transition pressure P_t (GPa) II→V	Onset: 13.2 ± 0.2 Completion: 16.4 ± 0.5	~ 16	$14.3,$ ^b 12.0 ^c
Lattice parameters a, c (Å) phase V (~ 16 GPa)	$a = 2.551 \pm 0.006$ $c = 2.387 \pm 0.007$	2.527 2.373	$a = 2.400, c = 2.297$ ^b $a = 2.561, c = 2.446$ ^c (Values at 12 GPa)
c/a ($P \sim 16$ GPa)	0.936 ± 0.005	0.937	$0.957,$ ^b 0.955 ^c (Values at 12 GPa)
Volume V_t (Å ³ /at.) phase V ($P = P_t \sim 16$ GPa)	13.45 ± 0.10	13.12	$13.23,$ ^b 13.5 ^c
Bulk modulus (GPa) phase V	310 ± 30		

^aReference 10.

^bReference 27.

^cReference 28.

tion, reporting an onset of 8.8 GPa, indicative of non-hydrostatic conditions. These authors gave no details of lattice parameters.

A comparison between various experimental and theoretical parameters is included in Table III. Most interesting is the comparison with Yin and Cohen²³ and Needs and Martin²⁷ who used *ab initio* band-structure calculations to generate the total energy of the crystal as a function of volume. The values of the lattice parameters are close to the experimental values, but both groups find a lower transition pressure than the experimental values. This is discussed further in Sec. IV.

Jamieson⁸ observed extra lines ($d = 2.613$, and 1.713 Å) in his x-ray-diffraction record of phase II. The estimated pressure for his experiment with phase II was 16 GPa, but this pressure probably corresponds to $\lesssim 13$ GPa using the ruby fluorescence scale, since at 16 GPa, phase V should predominate. The persistence of some of the diffraction lines in Jamieson's experiment after release of pressure indicates that phases II and III were present in his sample volume. No trace of phase III was found in the present experiments while pressure was increased, or even held at 13 GPa for several days. This implies that a fairly large pressure gradient was present across Jamieson's Si sample, and that part of the sample (probably those parts furthest from the axis of the anvils) initially converted to phase II on increase of load, then converted to phase III as the pressure locally fell below ~ 8.5 GPa due to sample flow. This result is consistent with Jamieson's setup³⁷ where x rays pass parallel to the anvil faces since diffraction information is obtained from crystal planes that are subject to a large pressure gradient.

C. II-V transition and phase V

The onset of the transition from Si(II) to Si(V) was observed at 13.2 ± 0.2 GPa (Ref. 11). The crystal structure of Si(V) was identified as simple hexagonal, with lattice parameters $a = (2.551 \pm 0.006)$ Å, $c = (2.387 \pm 0.007)$ Å. Data for phase V and II-V transition are listed in Table III.

Olijnyk *et al.*¹⁰ also concluded that the structure of Si in this region was primitive hexagonal. Small differences

are to be noted between the two experiments. Firstly, the relative volumes found by us up to 25 GPa are slightly higher than those of Olijnyk *et al.*,¹⁰ while reasonable agreement is recorded for phase II. The origin of this discrepancy is not clear. The absolute error in the values of lattice parameters a and c for phase V were estimated to be ± 0.006 Å, so that $\Delta V/V_0$ is calculated to a precision of $\pm 0.3\%$. Differences in volume between the present results and those of Olijnyk *et al.*¹⁰ amount to $\geq 1\%$ in this pressure region.

Figure 1, taken from Needs and Martin,²⁷ illustrates the structure of Si(II) and Si(V), and the calculated atomic displacements needed to affect the transition. Note that in the body-centered-tetragonal structure, the coordination

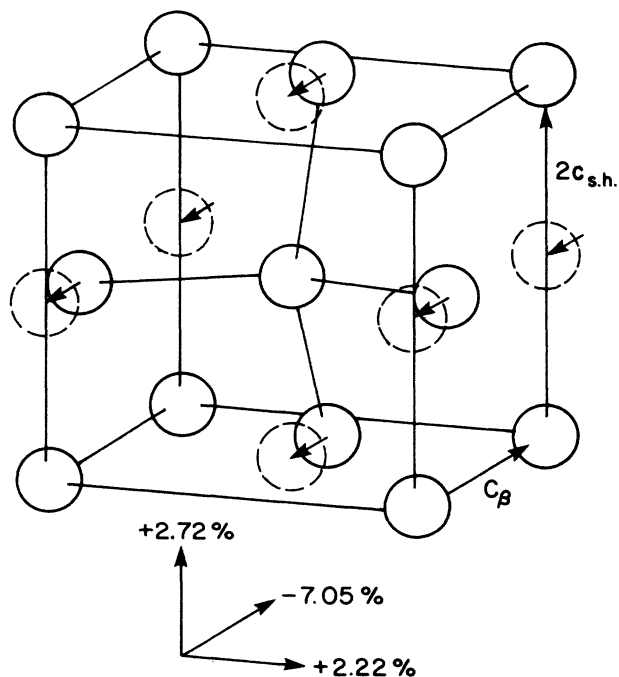


FIG. 1. A sketch of the unit cells for Si(II) and Si(V), reproduced with permission from Needs and Martin (Ref. 27). The arrowed percentages indicate the calculated lattice distortions for II→V.

TABLE IV. Experimental and theoretical data for phase VII (hcp) (Si).

Parameter	Present experiment	Experiment of Olijnyk <i>et al.</i> ^a	Theory
Transition pressure P_t (GPa)	~36–42	~42	41 ^{b,c} 41 ^b
Lattice parameters ^d a, c (Å)	$a = 2.524 \pm 0.009$ $c = 4.142 \pm 0.05$	2.444 4.152	2.469 ^e 4.185 ^e
c/a ^f	1.64 ± 0.02	1.70	1.67 ^e 1.695 ^e
V^{VII} (Å) ³ /at. ^d	11.4 ± 0.2	10.7	11.02 ^e
V^{V} (Å) ³ /at. ^d	12.3 ± 0.2		11.96 ^e

^aReference 10.

^bThese authors calculate the transition pressure for $\beta\text{-Sn} \rightarrow \text{hcp}$.

^cReference 24.

^dAt 41–42 GPa.

^eReference 28.

^fBased on extrapolation of data.

can be viewed as sixfold, since at 12 GPa there are four nearest neighbors at a distance of 2.43 Å and two next-nearest neighbors at a slightly greater distance $c = 2.58$ Å. Similarly, the hexagonal structure can be viewed as eightfold with six atoms on the basal plane and two atoms at a slightly shorter distance c (Table III). Thus the coordination number increases from 4→6→8→12 when the pressure is increased.

An increasing trend was found in the c/a ratio of phase V with pressure. Data are plotted in Fig. 2 as c/a versus atomic volume to compare directly with the calculation of Needs and Martin²⁷ and Chang and Cohen,²⁸ and with the data of Olijnyk *et al.*¹⁰ The trend is similar, but the experimental values lie somewhat lower than the theoretical.

D. Phase VII and the V→VII transition

Data for phase VII (Table IV) indicate differences between the present data and those of Olijnyk *et al.*¹⁰ The atomic volumes differ by ~6%, most of this difference being accounted for in the lattice parameter a . The

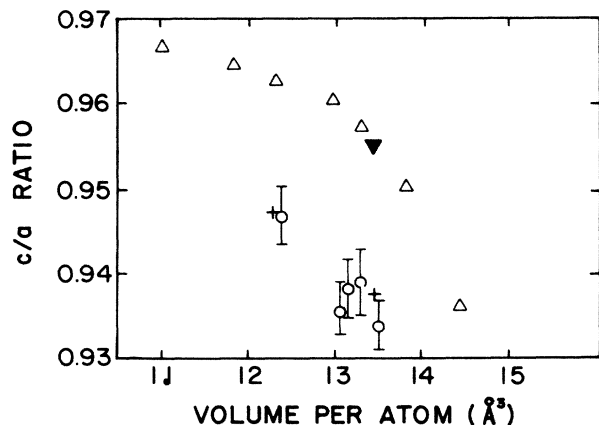


FIG. 2. The c/a ratio for phase V as a function of atomic volume. \triangle , theory (Ref. 27); \blacktriangledown , theory (Ref. 28); +, experiment (Ref. 11); \circ , present experiment with error bar indicated.

reasons for these discrepancies are not known.

The transformation from the primitive hexagonal to hexagonal-close-packed structure can be accomplished by sliding each plane of atoms with respect to the next. In the process, the a parameter does not change appreciably. [Extrapolated to ~42 GPa, $a_V \sim 2.46$ Å, compared to $a_{\text{VII}} = 2.524$ Å, so that a slight (~2%) expansion occurs.] The c parameter decreases by ~10%. It is to be expected that such a large shear would lead to high densities of dislocations and planar defects in the two-phase region, accounting for the diffuse background observed between ~36.5 and 42 GPa. Olijnyk *et al.*¹⁰ concluded that a new phase (VI) exists in this region. Their notation for phases is followed in this paper to avoid confusion, but no evidence is presented in this paper for a new phase, nor is evidence presented against its existence.

E. V→II and II→III transitions on decompression

Experiments confirmed the sequence V (14.5 GPa) → II + V (11 GPa) → II (10.8 GPa) → II + III (8.5 GPa) → III for stepwise decompression over a period of days. Table V lists the lattice parameters obtained in the present work for BC 8 phase (III), which is metastable at atmospheric pressure.^{2,13} The x-ray-diffraction lines for III were broad, indicating a strained lattice.

IV. DISCUSSION

This paper presents data for phases of Si which can be compared directly with *ab initio* calculations.^{22–28} It is gratifying to note the good overall agreement between theory and experiment, and the ability of this theory to predict new phases.

X-ray data have been presented for the Si(I)→Si(II) transition under close-to-hydrostatic conditions, and the effects of shear stresses have been examined. It is important to point out that comparison of experimental and theoretical transition pressures must be made with caution. Firstly, the theoretical results are obtained for $T = 0$ K. Secondly, experimental transition pressures are not to be equated with (thermodynamic) equilibrium pressure,

TABLE V. Data for phase III and V→II and II→III transitions or decrease of pressure.

Parameter	Present work	Other work
$P_t(\text{V} \rightarrow \text{II})$ (GPa)	14.5–11 (phases V + II present)	
$P_t(\text{II-III})$ (GPa)	10.8–8.5 (phases II + III present)	
Lattice parameter (Å) phase III at P_t (~10 GPa)	6.405±0.005	
Lattice parameter (Å) phase III at $P=0$	6.62±0.01	6.636±0.005 ^a 6.67 ^b
Bulk modulus (GPa)	6.66±0.03	96 ^b

^aReference 13.^bReference 26.

because kinetic factors are involved. If a complete hysteresis loop (I→II→I) could be obtained, an estimate for the equilibrium pressure could be made. However, this is not possible for Si since the metastable phase III is produced on release of pressure. The only III-V compound on which a complete hysteresis loop has been obtained is InAs using x-ray-diffraction data.³⁸ From these data it is reasonable to conclude that transition pressures on increase of pressure may be overestimated by 2 GPa or more. For Si the equilibrium transition pressure will be less than or equal to the onset pressure under hydrostatic conditions. No quantitative statement can be made relating the equilibrium pressure to the onset pressures obtained experimentally with either hydrostatic pressure, or with shear stresses present.

It is interesting to inquire whether phase III is a thermodynamically stable phase between phases I and II. If so, the fact that III is not observed on increase of pressure would be due to kinetic factors, as would the persistence of phase III to room pressure. However, Yin²⁶ has calculated that phase III for Si is indeed metastable over the whole pressure range. His models permitted atoms to be shifted in various directions, indicating that phase III of Si is formed metastably from II on decrease of pressure because it is easier for atoms to move in the direction towards Si III, rather than towards the thermodynamically stable structure I.

The present work has been carried out with higher precision and accuracy (see Ref. 30 for a discussion) than the

earlier work of Jamieson,⁸ whose values for volume changes at the transition were quoted by Van Vechten.²⁰ Van Vechten used the volume-ratio $[V^{\text{I}}(P_t) - V^{\text{II}}(P_t)]/V^{\text{I}}(P_t) = 0.209$ for Ge, Si, and Sn as a cornerstone of his calculation for the transition pressures of the group-IV elements and III-V compounds. This work was important, in that it stimulated many high-pressure studies of these materials, including the present one. However, the present data (see also Ref. 38 for similar data on III-V compounds) do not support his scaling relationship for the volume changes. The new *ab initio* calculations of Si and Ge (Refs. 22–28) indicate that high-pressure behavior can be predicted accurately, and it is hoped that such work will be extended to III-V, II-VI, and other compounds.

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