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New high-pressure phase of Si

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Angle-dispersive powder-diffraction techniques utilizing an image-plate area detector have been used to reexamine the high-pressure behavior of silicon to ~18 GPa. We have observed a new intermediate body-centered orthorhombic structure between the well-known Si II (β-tin) and Si V (simple-hexagonal) structures. The existence of such a phase has been considered previously in energy calculations, and may pertain to the observed pressure dependence of the superconducting transition temperature of Si in the 13–18 GPa range.

I. INTRODUCTION

The high-pressure behavior of silicon has been the subject of intense experimental and theoretical interest for 30 years.[1] Diffraction studies have been made at pressures in excess of 240 GPa, and ten different crystal structures are known.

On increasing pressure, Si transforms from the cubic diamond structure to the β-tin structure (Si II) at ~12 GPa.[2–4] At ~16 GPa, Si II transforms to Si V which has a simple-hexagonal structure,[3,4] the first observation of such a structure in an elemental system. At 37.6 GPa, Si V transforms into the so-called intermediate phase (Ref. 3), Si VI, which is thought to have the same crystal structure as the X phase of the alloy $Bi_{0.8}Pb_{0.2}$ (Ref. 5). Si VI transforms to hcp Si VII at 42 GPa,[3] which subsequently transforms to fcc Si at 78 GPa.[6]

On pressure decrease, four further phases are known, all metastable at atmospheric pressure. Si III, also known as the BC8 phase, has a body-centered cubic structure,[7] and is obtained on relatively slow decompression from Si II. On heating, Si III transforms to Si IV (Ref. 8) which has the (hexagonal) wurzite structure. On very fast decompression of Si II to atmospheric pressure, two tetragonal phases have been found[9] and designated Si VIII and Si IX.

The abundance of experimental studies, especially the observation of simple-hexagonal Si V and metastable Si III, has stimulated a large number of theoretical studies.[10–19] These have been concerned mostly with understanding the relative stability of the various structures through total energy calculations, while band-structure calculations led to the prediction of superconductivity in the high-pressure phases.[20] This was subsequently confirmed experimentally, and a superconducting transition temperature in the range 4–8 K has been measured by several authors to 45 GPa.[21–26]

In this paper we report the observation of a new body-centered orthorhombic structure of silicon occurring at high pressure *between* the β-tin Si II and simple-hexagonal Si V phases. Such a phase has previously been considered theoretically,[15,17] and we speculate that it may have some bearing on the pressure dependence of T_c observed in the range of 13–18 GPa.[21–26]

II. EXPERIMENTAL TECHNIQUES

The x-ray diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury, using angle-dispersive powder-diffraction techniques and an image-plate area detector. The incident wavelength was 0.4446(1) Å. Considerable care was taken to minimize the background level and possible contaminant features in the powder patterns (gasket lines, for example). The two-dimensional powder patterns recorded on the image plate were integrated to give conventional 1-d profiles. Details of our beamline setup, experimental procedures and pattern integration program have been published separately.[27,28]

The finely powdered sample was prepared from starting material of 99.9999% purity. Three separate experiments were performed using a Diacell DXR-4 diamond-anvil cell[29] which has a full conical aperture of half-angle 50°. The pressure-transmitting medium was a 4:1 mixture of methanol:ethanol. Sample pressures were determined from the previously measured compressibility of silicon.[3,4] The structural results described were all obtained by full Rietveld[30] refinement of the integrated profiles, using the program MPROF.[31]

III. RESULTS AND DISCUSSION

On pressure increase we observed the well-known metallization transition from Si I to Si II at 10.3 GPa. Multiphase Rietveld refinement of a pattern from a 50:50 mixture of Si I-Si II gave unit-cell dimensions of $a=5.277(1)$ Å for Si I and $a=4.665(1)$ Å, $c=2.572(1)$ Å for Si II, and hence a volume decrease of 23.8(2)% at the transition. This is a slightly higher value than the ~22.5(5)% reported from previous measurements.[2,4,32] (We believe our value to be more accurate as it is from a multiphase Rietveld refinement of a full diffraction pattern.) The β-tin phase suffers from very strong preferred orientation, as previously found by Jamieson.[2] In addition, we observe that some peaks, especially the (200), are broadened significantly relative to the other observable β-tin peaks in the pattern [Fig. 1(a)]. We have seen similar broadening in our studies of the β-tin phase of InSb.[33]

On increasing pressure, a change in the diffraction pattern was observed in all three experiments to a new pattern [Fig. 1(b)] containing extra reflections that are not compatible with the simple-hexagonal Si V structure. This transition was also characterized by a shift of the first strong reflection in the pattern to a smaller 2θ angle (longer d-spacing). This shift has been observed previously at 13.2(2) GPa by Hu and Spain[4] who ascribed it to a transition to a mixed Si II-Si V phase which existed to 16.4(5) GPa.

Further slight pressure increases in two of the samples (the third sample would not go above ~15 GPa) resulted in the disappearance of the extra reflections, and the appearance of the simple-hexagonal Si V phase which is shown in Fig. 1(c). Rietveld refinement of this pattern, including a correction for severe preferred orientation, gave unit-cell dimensions of $a=2.539(1)$ Å and $c=2.380(1)$ Å.

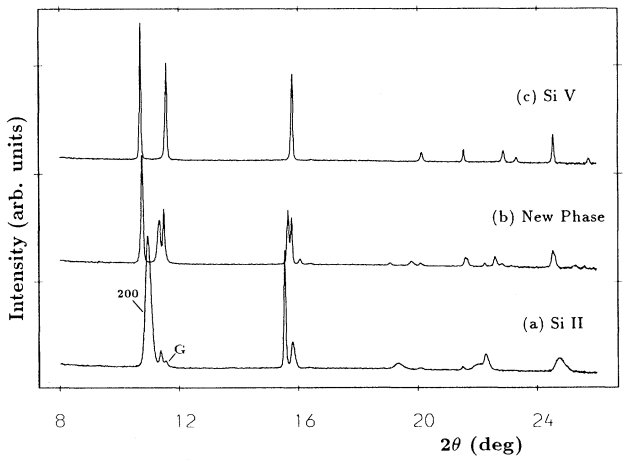

FIG. 1. The integrated profiles of patterns recorded from silicon on pressure increase. (a) The β-tin Si II phase, (b) the new phase, and (c) the simple-hexagonal Si V phase. The broadened (200) reflection in the Si II profile is indicated, while a weak peak arising from the tungsten gasket is labeled "G." In all three profiles, $\lambda=0.4446$ Å, and the sample-plate distance=350 mm. The exposure times were ~40 min (a) and ~20 min [(b) and (c)].

On decreasing the pressure slightly from the simple-hexagonal phase, the reverse sequence was observed, with the extra lines again appearing in the diffraction pattern before further pressure decreases resulted in a transition back to Si II. Repressurizing one of the Si II samples back to Si V and then downloading again to Si II confirmed that the extra reflections appear on both pressure increase and decrease.

Attempts were first made to fit the new pattern with a two-phase mixture of Si II and Si V, the previously known phases in this pressure range. The results were very unsatisfactory; Fig. 2 shows the most nearly fitting Si II and Si V mixed profile we could find. It can be seen that (220), (231), and (420) reflections of the β-tin phase (labeled in Fig. 2) are not observed in the data, while many of the observed reflections (indicated by asterisks in Fig. 2) are not accounted for by either the β-tin *or* the simple-hexagonal phases. The relative volumes of the Si II and Si V unit cells used in the profile of Fig. 2 were also found to differ by 6%, two to three times the difference observed previously between pure phases of Si II and Si V.[3,4] This reflects the fact that the Si II component in Fig. 2 has a unit-cell volume *larger* than that measured in the pure Si II phase at lower pressures. The results thus suggest the presence of a new phase of silicon, reproducibly obtained on both pressure increase and decrease, *between* the Si II and Si V phases.

Unit-cell indexing, using DICVOL[34] and TREOR90,[35] determined that all the lines of the new phase could be indexed on a body-centered orthorhombic cell with dimensions $4.74\times4.50\times2.55$ Å^3. The unit-cell volume per atom (13.6 Å^3) is thus intermediate between that of Si II (14.0 Å^3) and Si V (13.3 Å^3). Analysis of the diffraction

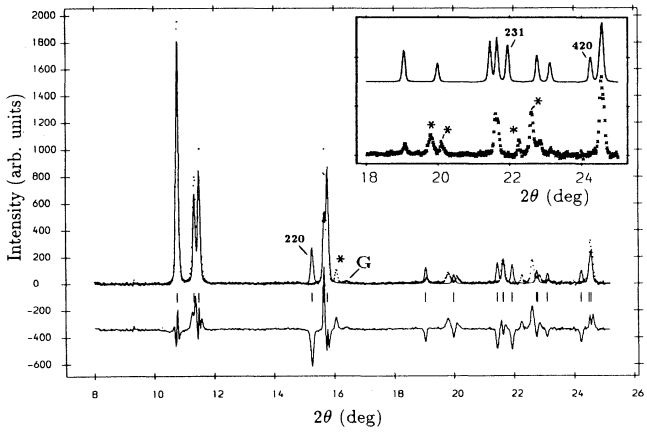

FIG. 2. A multiphase Rietveld refinement of the profile in Fig. 1(b), assuming a mixture of Si II and Si V. The crosses mark the observed data while the solid line is the calculated best fit. The tick marks show the positions of all reflections allowed by Si II and Si V. The difference between the observed and calculated profiles is shown below the tickmarks. G is a weak tungsten gasket line. The high-angled part of the pattern is enlarged in the inset, with the observed (bottom) and calculated (top) profiles separated for clarity. Si II reflections not observed in the data are indexed, while observed reflections not accounted for by the mixed-phase pattern are marked by an asterisk.

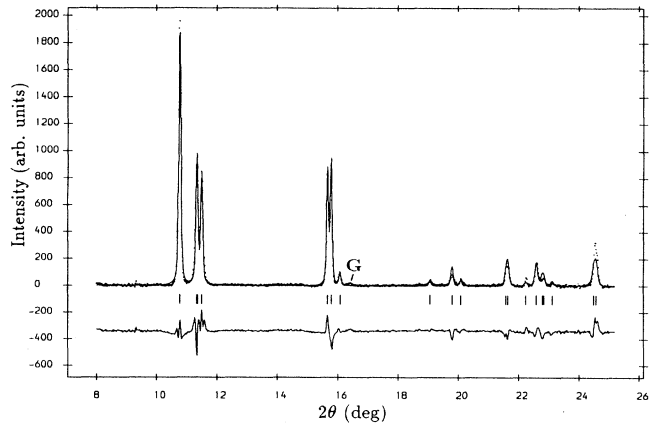

FIG. 3. The fit to the profile in Fig. 1(b) using the Imma structure. The tickmarks show the positions of all reflections allowed by symmetry. The difference between the observed and calculated profiles is shown below the tickmarks. G is a weak tungsten gasket line.

data showed the systematic absences to be consistent with space-groups Imma or Im2a. A trial structure was constructed with atoms in the 4(e) positions of Imma at $(0,\frac{1}{4},z)$ with $z\sim 0.2$ and was found to give calculated intensities in close agreement with the observed data. [This spatial arrangement is not distinguishable from the 4(b) positions $(\frac{1}{4},y,z)$ of space-group Im2a, but we assign the phase to Imma as it has the higher symmetry and is a maximal nonisomorphic subgroup of the β-tin space-group $I4_1/amd$.] A full Rietveld refinement of the pattern, including a correction for preferred orientation, is shown in Fig. 3, and gives $z=0.193(2)$, with unit-cell dimensions $a=4.737(1)$ Å, $b=4.502(1)$ Å, and $c=2.550(1)$ Å.

The structure of the new phase is shown in Fig. 4. We propose to label it as Si XI assuming the fcc phase at 78 GPa is Si X. To allow a direct comparison with the structures of Si II and Si V, the origin has been moved from its standard position in Imma, such that the atoms are at (0,0,0), $(0,\frac{1}{2},\Delta=2z)$ plus the body-center-related positions. The parameter Δ then indicates the height of the atom in the face of the unit cell. When $a=b$ and $\Delta=\frac{1}{4}$, the structure becomes the same as β tin, while if

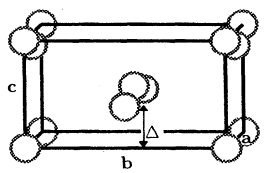

FIG. 4. The proposed structure of the new phase of silicon. The unit cell is orthorhombic, space-group Imma, with atoms in the 4(e) positions at $(0,\frac{1}{4},\Delta/2)$ or $(0,\frac{1}{2},\Delta)$ relative to the origin chosen here. The space-group origin has been moved from its standard position to facilitate comparison with the structures of Si II and Si V: when $a=b$ and $\Delta=\frac{1}{4}$, the Imma structure is the same as Si II, while if $b=\sqrt{3}c$ and $\Delta=\frac{1}{2}$, it becomes the same as Si V.

$b=\sqrt{3}c$ and $\Delta=\frac{1}{2}$, the structure is the same as simple hexagonal. The new structure can thus be seen as a natural intermediate step between the Si II and Si V structures. Furthermore, it is the monatomic equivalent of the body-centered orthorhombic structure that we have recently assigned to InSb II (with $\Delta\sim\frac{1}{2}$),[33] and that has been reported as the structure of GaAs III.[36]

The Imma structure, although not explicitly described as such, has been considered on theoretical grounds by Chang and Cohen,[17] and by Needs and Martin.[15] In both cases, the Si II-Si V transition was described in terms of soft phonon modes in Si II resulting in a displacement of half the atoms $\frac{1}{4}$ of a unit cell along the z axis. Chang and Cohen[17] found that the energy barrier between the β-tin and simple-hexagonal structures for such a transition mechanism was negative—i.e., no energy barrier, for certain values of the c/a ratio.

Needs and Martin[15] explicitly explored the case of intermediate orthorhombic structures. They calculated the total energy for five crystal structures along the path from β tin to simple hexagonal, choosing the four structural parameters (the unit-cell dimensions a, b, and c, and the z coordinate of the atom between $\frac{1}{4}$ and $\frac{1}{2}$) to change linearly between their values at the end points. Such structures have space-group Imma. They found that any energy barriers, if present, would be smaller than 0.01 eV/atom and concluded that "the continuum of structures along the path are potentially stable phases." They also suggested, in agreement with Chang and Cohen,[17,20] that the phonons near the Si II-Si V transition would be soft, and that this would enhance the superconductivity.

In light of this suggestion, it is of interest to examine the T_c measurements in Si to see if there is any evidence of the newly proposed phase. A reproducible feature of the P versus T_c measurements in the region of the Si II-Si V transition is the observation of a discontinuous jump in T_c at a pressure of ~ 13 GPa (Refs. 21, 22, and 26) (15 GPa in Ref. 24), followed by a gradual increase in T_c to a maximum at a pressure of ~ 15 GPa (Refs. 22 and 26) (17 GPa in Ref. 24). We speculate that the discontinuous jump at ~ 13 GPa may be indicative of the Si II-Imma transition, while the maximum in T_c is reached at the Imma-Si V transition. Theoretical calculations taking account of the Imma structure, and combined T_c and diffraction measurements in the 13–18 GPa region, are required to test this possibility. [We would note that similar changes in T_c at pressures in the range 37–45 GPa (Ref. 23) are almost certainly due to transitions to, and from, the Si VI phase.[5]]

In conclusion, the high resolution and data quality obtainable using angle-dispersive diffraction techniques have enabled us to observe a new high-pressure phase of silicon existing between the well-known β-tin (Si II) and simple-hexagonal (Si V) phases. The new phase has a body-centered orthorhombic structure, space-group Imma, and is a natural intermediate structure between those of Si II and Si V. Observation of this new phase supports total energy calculations which suggested that such a structure could be stable.

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