

The Boron-Silicon Solid Solution: A Structural Study of the $\text{SiB}_{\sim 36}$ Composition

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The structure of a crystal of a solid solution of silicon in β -rhombohedral boron has been studied by single-crystal X-ray diffractometry. The final R value was 5.4% for 815 reflections. The space group is $R\bar{3}m$ and hexagonal lattice parameters are $a = 11.01(1)$, $c = 23.90(2)$ Å. The cell contains 305.51 boron and 8.443 silicon atoms. The boron framework of β -boron is only slightly changed. Two Si atoms occupy interstitial holes. A third silicon substitutes partially for a framework boron atom. The results obtained are discussed.

Introduction

Considerable work has been done in recent years in the elucidation of detailed structures and stoichiometries of a number of boron-rich phases. Many of these phases can be considered as derivatives of α - and β -rhombohedral boron, tetragonal boron, and boron carbide. The lattice of β -rhombohedral boron with a loose three-dimensional framework of boron atoms seems to be particularly adapted to form such boron-rich phases.

The study of the silicon-boron system has given rise to at least three well-established phases: SiB_4 , SiB_6 , and " SiB_{14} ." The first two phases were reported in the original work of Moisson and Stock (1), and later corroborated by other authors (2-4). The phase " SiB_{14} " was first prepared by

Giese *et al.* (5) who reported for it trigonal symmetry and cell parameters similar to β -rhombohedral boron. On the basis of density, space group, and cell volume these authors concluded that silicon could be substituted in the β -boron structure.

It is presently known that a number of metals do form solid solutions with β -boron and are accommodated interstitially in the holes of the open boron framework. This is the case of $\text{CrB}_{\sim 41}$ (6), $\text{CuB}_{\sim 28}$, and $\text{MnB}_{\sim 23}$ (8), $\text{ScB}_{\sim 28}$ (9), $\text{ZrB}_{\sim 51}$ (10), and $\text{FeB}_{\sim 49}$ (11).

More recently Viala *et al.* (12, 13) have prepared a phase corresponding closely to a SiB_{14} composition and on the basis of accurate density and Si content data have concluded that silicon addition into the β -boron lattice follows a more complex behavior than simple substitution or insertion.

In order to elucidate the structure of this phase and show how the silicon atoms are accommodated in the β -boron lattice, it seemed relevant to carry out a detailed X-ray analysis on this phase.

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Experimental

1. *Synthesis and characterization.* Homogeneous mixtures of boron (alfa, 99.7%) and silicon powders (Fluka, 99.9%) with compositions varying from 0 to 15 at.% Si were placed in a boron nitride crucible, fired for 1 hr at 1600°C under argon atmosphere, and then rapidly cooled. Powder patterns on the reaction products revealed two different fields in this composition range. From 0 to about 5.5 at.% Si a regular variation of the β -boron type cell parameters was observed. This corresponds to a single boron-silicon solid solution. At silicon contents greater than 5.5 at.% a two-phase region was observed, consisting of the above solid solution and SiB_6 . The variation of a_0 and V of the hexagonal cell as a function of initial Si content is given in Fig. 1. From these data, the maximum solubility of silicon in β -boron was found to be 5.6 ± 0.3 at.% at 1600°C (12).

Polycrystalline single-phase ingots have been prepared by crystallization from a

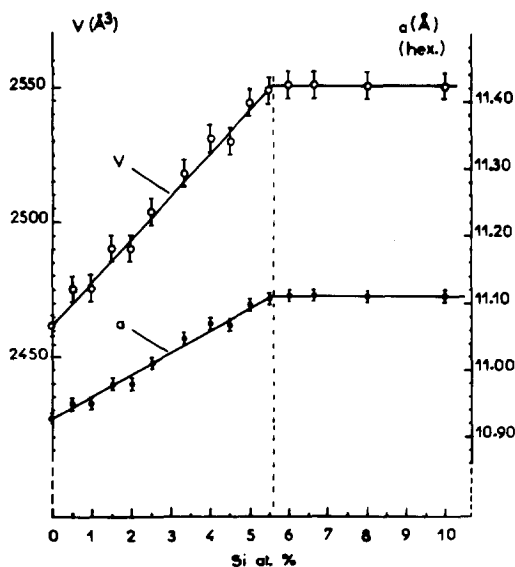


FIG. 1. Variation of the volume (\AA^3) and a_{hex} (\AA) of the hexagonal cell as a function of silicon content.

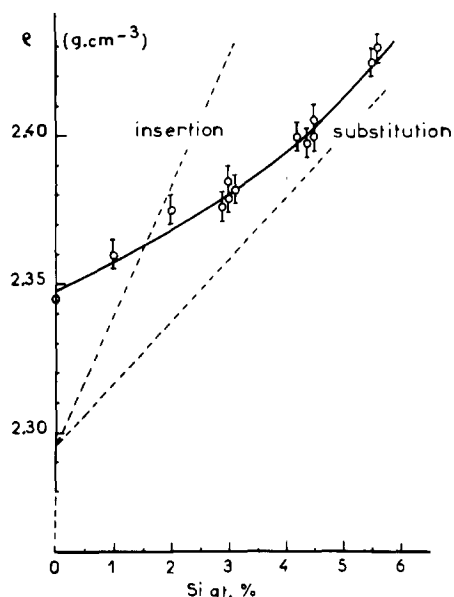


FIG. 2. Density vs silicon content (at.%) for samples obtained by the zone melting technique.

boron-silicon melt at about 2000°C using a zone-melting technique similar to the Verneuil method (13, 14). Electron microprobe analysis performed along these ingots has shown that a homogeneous and fixed distribution of silicon can be achieved in the middle third of the samples. A two-phase alloy with high silicon content was always found in the last third of the ingot.

The density of the bulk zone-melted samples of B-Si solid solution with various silicon contents has been measured either by a hydrostatic pressure method or by flotation in a $\text{CH}_3\text{Br}-\text{CCl}_4$ mixture. The results are given in Fig. 2. The theoretical densities of a B-Si solid solution in the case of a total substitution or a total insertion of silicon in the β -boron framework have also been plotted in the figure. A comparison of the theoretical and experimental curves tends to indicate a more complex hypothesis than either one of the simple structural mechanisms.

For the structural analysis, a single crystal was taken from a coarsely monocrystal-

line chip cut in the middle third of the zone-melted ingot. The silicon content of this chip determined by electron microprobe analysis was 2.74 ± 0.14 at.%. A density of 2.382 (8) g/cm^3 was found by flotation. This value is most probably an overestimate due to heavy impurities possibly present in the chip. From spark source mass-spectroscopic analysis performed on boron specimens prepared under the same conditions (14), the concentration of foreign elements in the crystal has been estimated to be lower than 6000 wt. ppm, with carbon and oxygen being the most abundant (≈ 3800 wt. ppm).

2. *Crystal data.* A preliminary study using Weissenberg and precession methods indicated a trigonal Laue symmetry $3m$. The systematic extinctions are compatible with the space groups $R\bar{3}m$, $R3m$, or $R32$. In the absence of contrary information and in agreement with the β -rhombohedral boron space group, the group $R\bar{3}m$ was retained for the analysis. This choice was corroborated, post facto, by the structure refinement. The cell parameters obtained from single crystal and powder data are $a = 11.01$ (1) and $c = 23.90$ (2) Å. They vary slightly from those reported by Giese *et al.* for "SiB₁₄" (5): $a = 11.13$, $c = 23.83$ Å. For comparison, the space group and parameters for pure β -boron are $R\bar{3}m$, $a = 10.925$ and $c = 23.814$ Å (15).

The calculated density for the cell containing 305.5 boron atoms and 8.44 silicon atoms corresponding to 2.689 at.% silicon (as established by the present X-ray analysis) is 2.342 g cm^{-3} . The experimental density for the solid solution at 2.689 at.% Si, read from Fig. 2, is 2.374 (8) g cm^{-3} . A single crystal with the shape of a silex and approximate dimensions 0.47×0.14 mm was mounted along the c -axis. The intensities were collected on a three-circle automatic diffractometer with a $\text{MoK}\alpha$ ($\lambda = 0.71069$ Å) radiation and a graphite monochromator. A scintillation counter and a

$\theta/2\theta$ multiple scanning technique with a scan rate of $10^\circ(2\theta)/\text{min}$ were used. In order to improve the statistics eight independent scans were made. A total of 832 independent reflections have been obtained after averaging the six equivalents measured up to $\theta_{\text{max}} = 45^\circ$. Only 815 had intensity $I > 3\sigma$ (1) and were considered to be observed. These intensities were corrected for Lorentz and polarization effects. No absorption correction was applied ($\mu_r = 0.028$).

3. *Determination and refinement.* The structure was solved by Fourier methods starting with a model corresponding to the framework boron atoms of the β -boron structure but not including B(16). A Fourier synthesis, calculated using this model, showed two additional electron density maxima. The first Si(1) corresponds to an interstitial hole A1 (Table III) previously occupied by a transition metal in metal- β -boron solid solutions (6-11). The second Si(2) corresponds to an available interstitial hole in the β -boron framework but never previously observed. The B(16) atom found in pure β -boron was not present in this structure.

A number of cycles of refinement showed that position B(1) had an abnormally low temperature factor and higher charge density than that corresponding to a boron atom. A silicon atom was assumed to be partially substituted in this site and its occupancy factor refined. The refinement results showed that silicon content in the lattice was greater than that found experimentally. It was concluded that the site was statistically occupied by both boron B(1) and silicon Si(3). The refinement continued with isotropic temperature factors and variable occupancy factors for B(1), B(13), Si(1), Si(2), Si(3), which all showed partial occupation, using a full-matrix least-squares program (16). Atoms B(13) and B(15) which had higher than normal temperature factors were then refined aniso-

TABLE I
 ATOMIC COORDINATES AND TEMPERATURE FACTORS OF SiB₋₃₆ WITH THEIR ESD

Atoms	Sites	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Occupancy (%)
B(1), Si(3)	36(<i>i</i>)	0.1709(2)	0.1757(2)	0.1771(1)	1.04(4)	B(1): 86.7(3) Si(3): 13.3(3)
B(2)	36(<i>i</i>)	0.3182(2)	0.2954(2)	0.1286(1)	0.74(3)	100
B(3)	36(<i>i</i>)	0.2611(2)	0.2171(2)	0.4196(1)	0.69(3)	100
B(4)	36(<i>i</i>)	0.2354(2)	0.2514(2)	0.3469(1)	0.67(3)	100
B(5)	18(<i>h</i>)	0.0544(2)	0.1088(2)	0.9441(1)	0.58(4)	100
B(6)	18(<i>h</i>)	0.0860(2)	0.1720(2)	0.0135(1)	0.57(4)	100
B(7)	18(<i>h</i>)	0.1106(2)	0.2212(2)	0.8875(1)	0.69(4)	100
B(8)	18(<i>h</i>)	0.1697(2)	0.3394(2)	0.0279(1)	0.65(4)	100
B(9)	18(<i>h</i>)	0.1299(2)	0.2598(2)	0.7658(1)	0.75(4)	100
B(10)	18(<i>h</i>)	0.1023(2)	0.2046(2)	0.6981(1)	0.64(4)	100
B(11)	18(<i>h</i>)	0.0567(2)	0.1134(2)	0.3269(1)	0.64(4)	100
B(12)	18(<i>h</i>)	0.0896(2)	0.1792(2)	0.3986(1)	0.59(6)	100
B(13)	18(<i>h</i>)	0.0585(2)	0.1170(2)	0.5538(1)	0.93(6)	73.9(6)
B(14)	6(<i>c</i>)	0	0	0.3857(2)	0.62(7)	100
B(15)	3(<i>b</i>)	0	0	$\frac{1}{2}$	1.41(14)	100
Si(1)	6(<i>c</i>)	0	0	0.1330(1)	0.46(7)	46.4(6)
Si(2)	18(<i>h</i>)	0.1091(8)	0.2182(8)	0.1001(6)	0.58(7)	4.84(20)

Atoms	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃ (Å ²) × 10 ²
B(13)	1.26(20)	U ₁₁	1.06(18)	0.69(32)	-U ₂₃	-0.08(15)
B(15)	2.44(60)	U ₁₁	0.44(34)	1.03(66)	0	0

tropically. The resulting *R* value was 5.4%. The atomic scattering factors were those of Cromer and Mann (17). A final difference synthesis revealed no further significant electron density maxima.

Observed and calculated structure factors are compared in a separate Table.¹ The atomic, thermal, and occupational parameters are given in Table I and the interatomic distances are presented in Table II.

¹ See NAPS document No. 03732 for 6 pages of supplementary materials. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiches are \$3.00. Outside of the U.S.A. and Canada, postage is \$3.00 for a photocopy and \$1.50 for a fiche.

Description and Discussion

Detailed descriptions of the β -rhombohedral boron structure have been given by Hoard *et al.* (18) and Callmer and Lundström (12). Briefer descriptions have been published by other authors (6, 7, 9).

A short description of the structure will be given however in order to facilitate the discussion. Figure 3 represents a partial view of the three-dimensional lattice of our solid solution SiB₋₃₆.

Topologically the structure of SiB₋₃₆ is similar to that of β -boron as far as the boron framework is concerned. The main differences arise from the partial substitution of the icosahedral B(1) atom by silicon (Si(3)) and the partial occupation of two interstitial holes by Si(1) and Si(2) silicon atoms. A further difference concerns the absence in the SiB₋₃₆ structure of B(16) whose pres-

TABLE II
INTERACTOMIC DISTANCES FOR SiB₋₃₆ (IN Å)

B(1)-B(1) ^a	1.829(4)	B(8)-2B(3)	1.803(3)
B(1)-B(1)	1.987(4)	B(8)-2B(4)	1.747(3)
B(1)-B(2)	1.890(3)	B(8)-B(6)	1.633(3)
B(1)-B(2)	1.887(3)	B(8)-B(10)	1.838(3)
B(1)-B(7)	1.898(3)	B(8)-Si(2)	2.077(10)
B(1)-B(9)	1.889(3)	B(9)-2B(1)	1.889(3)
B(1)-Si(1)	2.180(5)	B(9)-2B(2)	1.861(3)
B(1)-Si(2)	2.095(10)	B(9)-B(7)	1.799(3)
		B(9)-B(10)	1.701(3)
B(2)-B(1)	1.890(3)		
B(2)-B(1)	1.887(3)	B(10)-2B(4)	1.847(3)
B(2)-B(2)	1.842(4)	B(10)-B(8)	1.838(3)
B(2)-B(3)	1.727(3)	B(10)-B(9)	1.701(3)
B(2)-B(7)	1.804(3)	B(10)-2B(11)	1.795(3)
B(2)-B(9)	1.861(3)		
B(2)-Si(2)	2.128(10)	B(11)-2B(4)	1.860(3)
		B(11)-2B(10)	1.795(3)
B(3)-B(2)	1.727(3)	B(11)-2B(11)	1.873(3)
B(3)-B(4)	1.830(3)	B(11)-B(12)	1.825(3)
B(3)-B(8)	1.803(3)	B(11)-B(14)	1.773(3)
B(3)-B(12)	1.790(3)		
B(3)-B(13)	1.789(4)	B(12)-2B(3)	1.790(3)
B(3)-Si(2)	2.052(10)	B(12)-2B(4)	1.820(3)
		B(12)-B(11)	1.825(3)
B(4)-B(3)	1.830(3)	B(12)-2B(13)	1.885(4)
B(4)-B(4)	1.692(4)	B(12)-B(14)	1.736(3)
B(4)-B(8)	1.747(3)		
B(4)-B(10)	1.847(3)	B(13)-2B(3)	1.789(4)
B(4)-B(11)	1.849(3)	B(13)-2B(12)	1.885(4)
B(4)-B(12)	1.860(3)	B(13)-2B(13)	1.932(6)
		B(13)-B(14)	1.826(3)
B(5)-2B(5)	1.797(4)	B(13)-B(15)	1.702(3)
B(5)-B(6)	1.765(3)		
B(5)-2B(6)	1.758(3)	B(14)-3B(11)	1.773(3)
B(5)-B(7)	1.726(3)	B(14)-3B(12)	1.736(3)
B(5)-Si(1)	2.115(5)	B(14)-3B(13)	1.826(3)
B(5)-2Si(2)	2.089(10)	B(15)-6B(13)	1.702(3)
B(6)-B(5)	1.765(3)	Si(1)-6B(1)	2.180(5)
B(6)-2B(5)	1.758(3)	Si(1)-3B(5)	2.115(5)
B(6)-2B(6)	1.762(4)	Si(1)-3B(7)	2.165(5)
B(6)-B(8)	1.633(3)	Si(1)-3Si(2)	2.224(11)
B(6)-Si(2)	2.116(10)		
		Si(2)-2B(1)	2.095(10)
B(7)-2B(1)	1.898(3)	Si(2)-2B(2)	2.128(10)
B(7)-2B(2)	1.804(3)	Si(2)-2B(3)	2.052(10)
B(7)-B(5)	1.726(3)	Si(2)-2B(5)	2.089(10)
B(7)-B(9)	1.799(3)	Si(2)-B(6)	2.116(10)
B(7)-Si(1)	2.165(5)	Si(2)-2B(7)	2.116(10)
B(7)-Si(2)	2.116(10)	Si(2)-B(8)	2.077(10)
		Si(2)-Si(1)	2.224(11)

^a B(1) represents the site occupied simultaneously by B(1) and Si(3).

ence is probably not necessary for the stability of the boron framework.

As shown in Fig. 3 the lattice is composed of B₁₂ icosahedra, B₆ half-icosahedra, B₁₀ units, and single boron atoms. The combination of the B₁₂ and B₆ units gives rise to the quasispherical unit B₈₄ with its center at the origin of the cell (0, 0, 0) and its threefold axis along *c*-axis of the hexagonal cell. The B₈₄ unit consists of a central icosahedron at (0, 0, 0) (atoms B(5) and B(6)) linked to 12 half-icosahedra B₆ of two types. The first type (B₆) includes three down-pointed and three up-pointed units involving atoms B(1), B(2), B(9), and B(7). They form complete icosahedra by uniting with B₆ units of the same kind from neighboring B₈₄ groups. The six half-icosahedra of the second type (B'₆), involving atoms B(3), B(4), B(8), B(10), are linked to B₁₀ units. Each B₁₀ unit is further linked to two other B'₆ half-icosahedra from different B₈₄ groups. The B₁₀ and the three B'₆ units thus form a condensed triple icosahedron B₂₈. These interconnections through the B₆ half-icosahedra help to form the open but rigid framework of the SiB₋₃₆ structure. The single atom B(15) is found between two B₁₀ units. The hexagonal cell must then ideally contain 315 boron atoms (3[84 + (2 × 10) + 1]).

This open framework contains a variety of interstitial holes listed in Table III (6). Some of them have been observed to be partially occupied in β -boron derivative phases, while others have remained empty. Of the three holes A1, A2, A3, only A1 is likely to be occupied by metal atoms since it has the longest distances to its neighbors. A2 is the next most likely to be occupied and A3 is highly unlikely because of its small size. The occupation of holes F1 and F2 is improbable since they are of low symmetry and highly irregular distances with the neighbouring boron atoms.

In SiB₋₃₆ the Si(1) atom is found in the A1 hole occupied in a number of β -boron

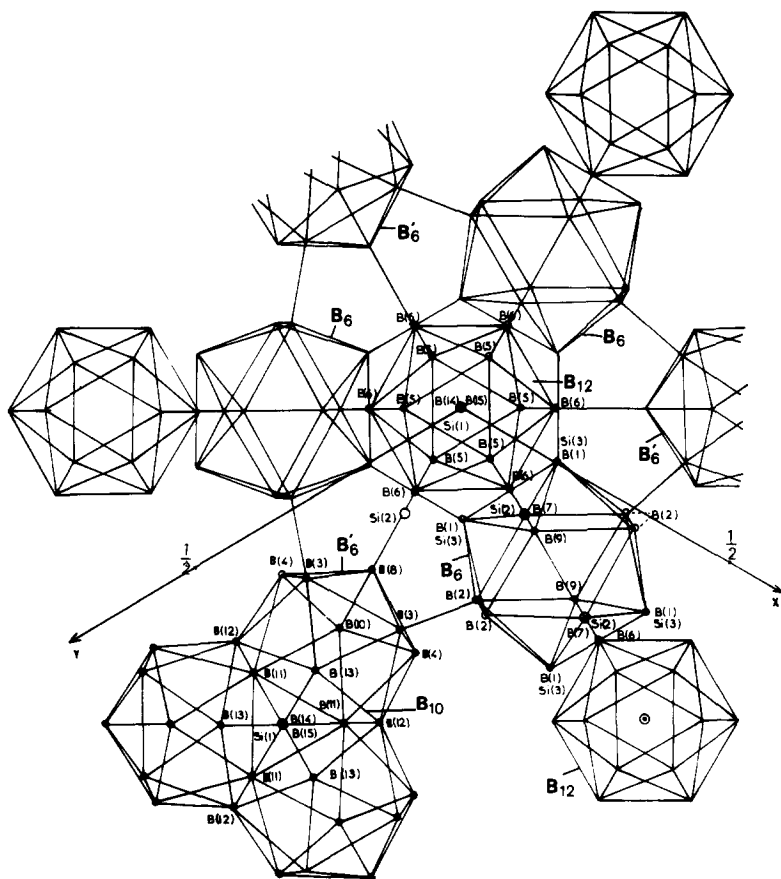


FIG. 3. Partial representation of the lattice. Overlapping entities are omitted for clarity. Black atoms indicate the B_{10} unit.

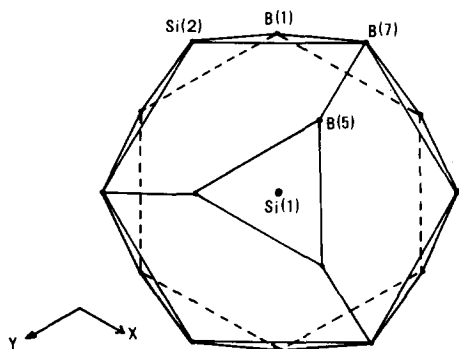


FIG. 4. Coordination polyhedron of the Si(1) atom situated in the A1 type hole.

phases by metal atoms. It has 12 boron neighbors at distances 2.115–2.180 Å and 3 further Si(2) at a distance of 2.224 Å. They are arranged in a tricapped truncated tetrahedron around Si(1) (Fig. 4). The Si(1)–B distances are slightly longer than the sum of their covalent radii ($r_{\text{Si}} + r_{\text{B}} = 1.11 + 0.88 = 1.99$ Å), whereas the Si(1)–Si(2) distance compares very well with that sum (2.22 Å).

Some Si(2) atoms are found in hole A2, never occupied before in any of the β -boron derivative structures (see Table III). The limited occupancy and the smaller radius of

TABLE III
AVAILABLE INTERSTITIAL SITES IN THE β -RHOMBOHEDRAL BORON NETWORK

Hole and approximate coordinates	β -B	Fe _{B-49}	Cr _{B-41}	Cu _{B-23}	Zr _{B-51}	Sc _{B-28}	Cu _{B-28}	Mn _{B-23}	Si _{B-36}
A1 0, 0, 0.135		Fe(1) 51% ^a	Cr(1) 72%	Cu(1) 8%			Cu(1) 6%	Mn(1) 26%	Si(1) 46%
A2 0.108, 0.216, 0.100									Si(2) 4.8%
A3 0.279, 0.248, 0.046									
D 0.205, 0.411, 0.174		Fe(2) 19%	Cr(2) 18%	Cu(2) 22%, 12%	Zr(2) 28%	Sc(2) 31%	Cu(2) 22%, 11%	Mn(2) 43%	
E 0, 0, 0.245				Cu(3) 61%	Zr(3) 18%	Sc(3) 73%	Cu(3) 51%	Mn(3) 66%	
F1 0.065, 0.130, 0.245									
F2 0.117, 0.233, 0.252									
G 0.055, 0.109, 0.117	B(16) 25%			B(16) 13%	B(16) 15%		B(16) 21%		

^a This figure indicates partial occupancy for all interstitial sites above.

Si(2) with respect to other metals probably makes the occupation of this hole possible. It has 12 boron neighbors at distances 2.052–2.128 Å and 1 Si(1) at 2.224 Å. They form a monocapped truncated tetrahedron around the silicon atom (Fig. 5). The silicon–boron distances are in this case

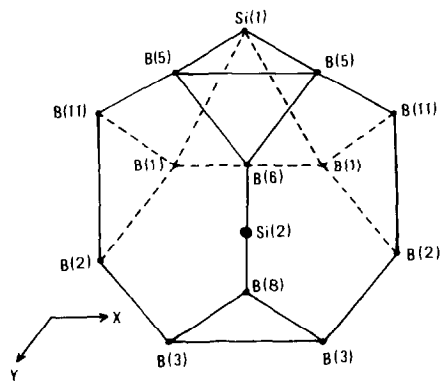


FIG. 5. Coordination polyhedron of the Si(2) atom found in the A2 type site.

slightly shorter than those observed for Si(1)–B, which corroborates the smaller size of the A(2) site. No other detectable interstitial position is occupied by a silicon atom.

The Si(3) atom was found to occupy, simultaneously with boron, the B(1) site. It is the first time that substitution was observed on the B(1) site of the framework. However, in ScB₂₈ another framework atom (B(4)) was shown to be substituted. Statistical distribution by both boron and silicon on the same site was also observed on a boron icosahedron in the case of SiB₄ (4). As can be seen from the distances to B(1) (Table II), and in particular from the B(1)–B(1) distance of 1.987 Å, this site is the most spacious one in the framework and the most likely to be occupied by an atom larger than boron ($r_{\text{Si}} + r_{\text{B}} = 1.99$ Å). Why there is this substitution and no further occupation of the interstitial holes could be explained by the electronic re-

quirements of the boron framework, the spherical symmetry, and the relatively large size of the silicon atom.

The absence of the B(16) atom in the β -boron structures seems to be partially controlled by the insertion of interstitial atoms in the A1 type hole (see Table III). It is the consequence of some very small distances between B(16) and the center of A1 (≈ 1.12 Å). In the case of SiB_{-36} the presence of Si on A1 (46%) would create an energetically very unfavorable situation. In the case of B(13) the boron occupancy of the site seems also to be partially controlled by the eventual presence of other atoms and their size in a D type hole (Table III). The maximum occupancy is observed for pure β -boron (73.4%) and SiB_{-36} (73.9%) where the D type hole is totally empty. Lower values are observed for CuB_{-23} (69%), ZrB_{-51} (53%), ScB_{-28} (61%), CuB_{-28} (61%), and MnB_{-23} (65%). Electronic requirements also play an important role.

In conclusion the introduction of silicon into the β -boron framework brings about only very minor changes. The variation in distances between β -boron and the silicon phase ranges from 0.001 to 0.083 Å with a mean of 0.024 Å.

The present solid solution, as determined by this analysis, corresponds to 2.689 at.% Si. This represents 305.51 boron atoms and 8.443 silicon atoms per unit cell. The value of 2.689 at.% Si compares well with that determined from the diagram showing a_{hex} vs at.% Si: 2.60(30) (Fig. 1).

A comparison of the calculated powder patterns for the three different mechanisms of silicon uptake into the β -boron lattice (substitution, insertion, and substitution-insertion) with the observed powder pattern for 1 at.% Si seems to indicate that

substitution is the most probably mechanism up to that level (1 at.% Si).

The limiting solid solution was observed to be about 5.6%. This limit is probably determined by competition between stabilization due to increase in entropy and decrease in electronic energy, and by destabilization caused by rising lattice-strain energy due to foreign atom substitution.

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