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A Single-Crystal Diffractometry Investigation of Scandium in β-Rhombohedral Boron

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The structure of a crystal of composition $ScB_{\sim 28}$ has been investigated using single-crystal diffractometry. The space group is $R\bar{3}m$ and the hexagonal axes are $a = 10.966$ Å and $c = 24.088$ Å. This is the structure of a solid solution of scandium in β-rhombohedral boron. The three-dimensional β-boron network is only slightly changed. The scandium atoms partially occupy three crystallographic positions. Two scandium atoms are inserted interstitially. The third scandium atom replaces two boron atoms at an intermediate position.

Introduction

The structure of the high-temperature modification of β-rhombohedral boron was determined by Hoard *et al.* (*1*). All 3*d* transition metals have been found to form solid solutions with β-boron. From X-ray powder data the cell expansion was measured and correlated to the microhardness (*2*). Detailed structure investigations by single-crystal studies have been carried out on samples of compositions $CrB_{\sim 41}$ (*3*), $CuB_{\sim 28}$ and $MnB_{\sim 23}$ (*4*), and $FeB_{\sim 49}$ (*5*). Chromium and iron atoms partially occupy two sets and copper and manganese atoms three sets of holes in the β-boron structure, none of the positions being fully occupied. From these structure investigations it can be concluded that the different distributions of the metals studied cannot be explained only on the basis of their different atomic sizes, as chromium and copper behave differently despite almost equal atomic radii. To supplement our knowledge about solid metal solutions in β-boron a detailed investigation of $ScB_{\sim 28}$ has been undertaken. The scandium solution is interesting since it displays a very large solution-hardening effect and the largest cell volume expansion of the 3*d* elements (*2*). Furthermore, scandium has a considerably larger atomic radius than the other 3*d* elements.

Experimental

Crystalline boron (Borax Consolidated, claimed purity 99.8%) and scandium metal (99.99%) were arc-melted and rapidly solidified under an atmosphere of purified argon. Samples with nominal compositions corresponding to $ScB_{12.3}$ and $ScB_{20.0}$ were prepared.

The sample with composition $ScB_{12.3}$ was examined by X-ray powder diffraction. A Guinier–Hägg focusing camera with Cu $K\alpha_1$ ($\lambda = 1.54051$ Å) radiation and silicon ($a = 5.43054$ Å) as an internal calibration standard was used. The unit-cell dimensions of the ScB_{12} phase were determined by a least-squares refinement with 24 measured 2θ values.

The sample with composition $ScB_{20.0}$ was examined with the technique mentioned above but using Cr$K\alpha_1$ ($\lambda = 2.28962$ Å) radiation and from this sample the single crystal used for

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TABLE I

UNIT-CELL DIMENSIONS OF $ScB_{\sim 28}$, β-BORON, AND ScB_{12}[a]

Axes	a (Å)	c (Å)
Hexagonal		
$ScB_{\sim 28}$ (single crystal)	10.9658(4)	24.0875(13)
$ScB_{\sim 28}$ (powder)[b]	10.9620(7)	24.0752(27)
β-boron (single crystal)[c]	10.9251(2)	23.8143(8)
β-boron (powder)[d]	10.9253(5)	23.8103(16)
Tetragonal		
ScB_{12} (powder)	5.2347(2)	7.3583(4)
ScB_{12} (single crystal)[e]	5.22	7.35

[a] Standard deviations are given in parentheses and refer to the last decimal place of the respective values.

[b] From Ref. (*2*).

[c] From Ref. (*10*).

[d] From Ref. (*3*).

[e] From Ref. (*12*).

collection of the intensity data set was taken. Cell dimensions of this single crystal were calculated from a least-squares fit of 2θ values from 17 reflections, the 2θ values being measured with a previously described technique (*4*).

The scandium content in the single crystal was measured with an electron probe microanalyzer (CAMECA MS 46) using the pure element as a standard and examining X-ray intensities from several points on the crystal surface. Corrections for the absorption, fluorescence, and atomic number effects were carried out (*6*). The scandium content obtained was 12 ± 2 wt% (3.2 at.%). The estimated maximum error includes the scattering of the measurements. The main contribution to the error arises from the roughness of the surface rather than the corrections.

Intensities were recorded with an automatic STOE–Philips four-circle diffractometer using monochromatized Mo$K\alpha$ radiation and the $2\theta/w$ technique and the background was measured on each side of the scanning interval, which was 1.60°. All reflections up to $2\theta = 60°$ with h, k, and $l \geqslant 0$ were measured. The crystal had a truncated rectangular pyramidal shape with the shortest edge 0.04 mm and the longest edge 0.11 mm, while the calculated linear absorption coefficient for Mo$K\alpha$ radiation was 7.8 cm^{-1}.

The crystallographic calculations were performed using IBM 370/155 and IBM 1800 computers and a list of the programs used is given in (*7*). The atomic scattering factors, taken from (*8*), were corrected for anomalous dispersion according to Cromer (*9*).

Phase Analysis and Crystal Data

Examination of the powder pattern showed that the $ScB_{20.0}$ sample contained a phase similar to the transition metal solid solutions of β-boron (*3–5*) and this phase is denoted here by $ScB_{\sim 28}$, which is the composition obtained from the single-crystal refinement described below. The hexagonal cell dimensions (space group $R\bar{3}m$) of the $ScB_{\sim 28}$ phase and pure β-boron as measured with powder and single-crystal methods are given in Table I. The agreement between the results from the powder and those from the single crystal are good, considering that systematic errors might be greater than the estimated standard deviations.

The $ScB_{20.0}$ sample was a two-phase specimen consisting of $ScB_{\sim 28}$ and ScB_{12}, while ScB_{12} was the majority phase in the sample of nominal composition $ScB_{12.3}$. ScB_{12} has been reported to have a fcc. UB_{12}-type structure with $a = 7.422 \pm 0.005$ Å (*11*), although a body-centered tetragonal structure has also been proposed (*12*) and has been confirmed (*13*). The accurate determination of the tetragonal cell parameters exclude the possibility of a cubic structure, so that the present result has established the tetragonal structure of ScB_{12}. The cell dimensions are given in Table I together with those of Ref. (*12*). Powder photograms of samples with nominal compositions between ScB_{12} and ScB_2 invariably displayed these two phases, and it was confirmed that ScB_2 belongs to the AlB_2-type structure in accordance with earlier results (*14*).

Two single crystals of the $ScB_{\sim 28}$ phase were checked for symmetry and crystal quality using the Weissenberg film technique. It was found that both crystals gave a few very weak diffuse diffraction spots in addition to the sharp reflections according to the requirements of the space group $R\bar{3}m$. The diffuse spots were all found in reciprocal lattice planes, situated perpendicular to the c^* axis and halfway between those r.l. planes containing the normal reflections. This observation suggests that ordering might occur, giving a small fraction of the unit cells a doubled c axis. The low intensity of the diffuse spots made them impossible to measure, so its was decided to ignore the diffuse spots in the refinement since they could have affected the determined structure only to a very small extent.

Refinement of the Structure

Intensities from 1243 reflections were measured and corrected for Lorentz and polarization effects and after averaging some of the F_0^2 values the data set consisted of 1031 independent structure factors (Table II). A difference synthesis was made from observed and calculated structure factors, the calculated structure factors being based on boron coordinates from β-boron (*1*) and metal coordinates from $MnB_{\sim 23}$ (*4*). The difference synthesis and the following refinements of the model did not reveal any evidence for a B(16) atom or an Me(1) atom, so these atoms were excluded from the model, which was refined to an R value of 7.5% ($R(F) = \Sigma||F_0| - |F_c||/\Sigma|F_0|$).

The function minimized was $\Sigma w(|F_0^2| - |F_c^2|)^2$, where $w = 1/[\sigma^2(F_0^2) + (C \cdot F_0^2)^2]$. $\sigma(F_0^2)$ was obtained from counting statistics. In the final refinement, described below, the best weighting scheme was obtained with $c = 0.035$. Structure factors for 314 reflections with $\bar{F}_0^2 < 2\sigma(\bar{F}_0^2)$ were given zero weights.

In a difference synthesis of the refined model a new low peak in electron density was found intermediate between two B(4) atoms, and this electron density was assigned to a new scandium atom Sc(4). Evidence for anisotropic behavior of Sc(2) was also found. Thus positional, occupational, and isotropic thermal parameters for Sc(4), and anisotropic thermal parameters for Sc(2), were refined. The short distance between B(4) and Sc(4) indicated that B(4) should have an occupancy of less than 100%, the occupancy being determined by refinement. Each of these modifications lowered the R value significantly according to Hamiltonian tests (*15*) based on weighted R values ($R_w(F^2) = [\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma w|F_0|^4]^{1/2}$. A refinement using anisotropic thermal parameters for all atoms gave no evidence of anisotropy except for B(15) and Sc(2). Anisotropic parameters for B(15) were included in the final refinement with a total of 63 parameters (one scale factor; positional parameters for 18 atoms; isotropic thermal parameters for B(1)–B(14), Sc(3), and Sc(4); anisotropic thermal parameters for B(15); and Sc(2) occupational parameters for B(4), B(13), Sc(2), Sc(3), and Sc(4)). The final R values were: $R(F) = 4.7\%$, $R(F^2) = 6.3\%$, and $R_w(F^2) = 8.4\%$, the final shifts all being less than 1% of the standard deviations. Coordinates and thermal and occupational para-

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (× 10) FOR $ScB_{\sim 28}$[a]

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Structure factors marked with an asterisk are those with $\bar{F}_0^2 < 2\sigma(\bar{F}_0^2)$.

meters are given in Table III, and interatomic distances are given in Table IV. In a final three-dimensional difference synthesis the largest deviation from zero was 7% of a boron peak in an F_0 synthesis.

The composition calculated from the result of the refinement was $ScB_{\sim 27.7}$ (3.5 at.% or 13.1 wt% Sc) as compared to the microprobe value $ScB_{\sim 30.5}$, mentioned earlier.

Discussion

A detailed description of the β-rhombohedral boron structure has been given by Hoard *et al.* (*1*), and brief and complementary descriptions have been given (*3*, *4*, *10*). Therefore, only the characteristic features of $ScB_{\sim 28}$ will be commented on below; however, a brief description of the β-boron structure is given in Fig. 1.

There are only small changes in the boron network of $ScB_{\sim 28}$, compared to the changes in that of β-boron (*10*). The changes are, however, more frequent and on the average are greater than those in similar structures studied earlier [$CrB_{\sim 41}$ (*3*), $MnB_{\sim 23}$ (*4*), $FeB_{\sim 49}$ (*5*), $CuB_{\sim 28}$ (*4*)], which might be expected from the large metal radius of scandium. The change in atomic coordinates displaces 9 boron atoms

TABLE III

STRUCTURE DATA FOR ScB$_{\sim 28}$[a]

Atom	Position	x	y	z	B (Å^2)	Partial occupancy (%)
B(1)	36(*i*)	0.17428(22)[b]	0.17305(23)	0.17433(8)	0.313(33)	
B(2)	36(*i*)	0.31847(24)	0.29386(23)	0.12889(8)	0.309(32)	
B(3)	36(*i*)	0.26165(24)	0.21742(24)	0.41839(9)	0.440(34)	
B(4)	36(*i*)	0.23783(26)	0.25242(26)	0.34743(9)	0.271(50)	92.5(10)
B(5)	18(*h*)	0.05411(17)	0.10822(17)	0.94334(12)	0.287(44)	
B(6)	18(*h*)	0.08460(17)	0.16920(17)	0.01299(12)	0.252(43)	
B(7)	18(*h*)	0.10827(17)	0.21655(17)	0.88852(12)	0.266(44)	
B(8)	18(*h*)	0.16859(18)	0.33719(18)	0.02772(12)	0.375(46)	
B(9)	18(*h*)	0.12986(17)	0.25973(17)	0.76774(12)	0.306(44)	
B(10)	18(*h*)	0.10172(17)	0.20345(17)	0.69826(12)	0.277(45)	
B(11)	18(*h*)	0.05810(17)	0.11620(17)	0.32820(13)	0.342(46)	
B(12)	18(*h*)	0.09033(17)	0.18067(17)	0.39764(12)	0.354(45)	
B(13)	18(*h*)	0.05585(30)	0.11170(30)	0.55603(22)	0.69(12)	61.3(14)
B(14)	6(*c*)	0	0	0.38524(22)	0.271(79)	
B(15)	3(*b*)	0	0	$\frac{1}{2}$	anisot.[c]	
Sc(2)	18(*h*)	0.20454(10)	0.40908(10)	0.17601(7)	anisot.[c]	31.4(3)
Sc(3)	6(*c*)	0	0	0.23539(5)	0.036(26)	72.7(5)
Sc(4)	18(*f*)	0.3713(10)	0	0	0.99(26)	5.7(3)

[a] Space group $R\bar{3}m$ (no. 166). Hexagonal unit cell dimensions: $a = 10.9658(4)$ Å, $c = 24.0875(12)$ Å, Cell volume; 2508.4 Å^3. (Rhombohedral unit cell: $a = 10.225$ Å, $\alpha = 64.85°$, $V = 836.1$ Å^3.)

[b] Standard deviations are given in parentheses and refer to the last decimal place of the respective values.

[c] Atom	B$_{11}$	B$_{22}$	B$_{33}$	B$_{12}$	B$_{13}$	B$_{23}$	B
B(15)	2.27(28)	2.27(28)	−0.04(28)	1.13(14)	0	0	0.271
Sc(2)	0.456(51)	0.456(51)	0.787(70)	0.000(56)	−0.357(29)	0.357(29)	0.667

B$_{ij}$ (in Å^2) is defined as $8\pi^2 U_{ij}$, where U_{ij} is the mean-square displacement tensor.

out of 15 by 0.035 Å–0.072 Å, and one half of the interatomic boron–boron distances are changed in comparison to the equivalent distances in β-boron at the 99.9% level of significance.

The changes in boron–boron distances range between 0.015 and 0.066 Å, the largest increase occurring for the B(9)–B(10) (0.066 Å) and the B(11)–B(11) (0.059 Å) distances, and the largest decrease for the B(5)–B(7) (0.056 Å), B(11)–B(12) (0.055 Å), and B(13)–B(13) (0.059 Å) distances.

In β-boron and in CuB$_{\sim 28}$, a sixteenth boron position is partially occupied, but in the present study no B(16) atom was found in the structure, despite the fact that there are no space restrictions on occupation of this position.

The metal atoms in ScB$_{\sim 28}$, Sc(2), Sc(3), and Sc(4) partially occupy three different crystallographic positions, which are shown in Fig. 1. The Sc(2) atom has 14 boron neighbors at distances from 2.36 to 2.46 Å (Table IV), the average being 2.42 Å. The shortest of these is 5% shorter than the radius sum 2.48 Å ($r_{\mathrm{Sc}} = 1.60$ Å, $r_{\mathrm{B}} = 0.88$ Å). The Sc(2) positions form a slightly puckered hexagonal ring, lying in the xy plane with B(15) at the center. The distance between the adjacent Sc(2) positions in the ring is 2.49 Å, which is 0.71 Å shorter

TABLE IV

Scandium–Boron and Scandium–Scandium Distances in ScB$_{\sim 28}$[a,b]

Sc(2)– B(13)	2.097(5)
– B(12)	2.356(3)
–2B(3)	2.387(3)
–2B(13)	2.403(3)
–2B(2)	2.427(2)
–2B(1)	2.439(3)
–2B(3)	2.446(3)
–2B(2)	2.453(2)
– B(15)	2.456(2)
–2Sc(2)	2.486(2)
Sc(3)–6B(1)	2.405(2)
–3B(9)	2.467(3)
–3B(11)	2.492(3)
–3B(10)	2.506(3)
Sc(4)–2B(4)	0.860(3)
–2B(8)	2.166(7)
–2B(3)	2.340(2)
–2B(10)	2.341(2)
–2B(11)	2.501(7)
–2B(12)	2.547(7)
–2B(4)	2.765(11)
–2B(6)	2.814(11)
–Sc(4)	2.822(18)

[a] In angstroms.

[b] Standard deviations in parentheses. Distances listed are Sc–B < 3.0 Å and Sc–Sc < 4.0 Å.

than the radius sum. Thus only three, nonadjacent positions can be occupied in a given ring (see Fig. 2).

One Sc(2)–B(13) distance is 2.10 Å, which is 0.38 Å (15%) shorter than the radius sum, but the Sc(2) and B(13) positions have an occupancy of 31% and 61%, respectively, so that the short distance need not actually occur in the structure. The short Sc(2)–B(13) distance, however, need not be the only reason for a partial occupancy of the B(13) position, since in *β*-boron only 73% of the B(13) positions are occupied. The occupancy of the B(13) position seems, in fact, to have decreased more than is necessary to avoid short Sc(2)–B(13) contacts.

The B(13) positions form a triangular antiprism with B(15) at the center and one triangular plane on each side of the hexagonal ring. The side of the triangle is short (1.84 Å) compared to the distance between the triangular planes (2.70 Å). The bonds between B(13) and B(15) are closer to the *c* direction than to the *xy* plane, and hence B(15) can be displaced in the *xy* plane more easily than in the *c* direction. The thermal parameters of

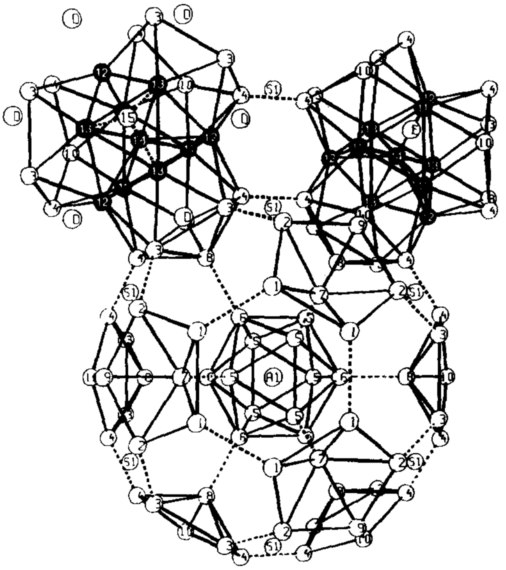

FIG. 1. *β*-Rhombohedral boron showing the B_{84} and B_{10} units of the structure viewed along the *c* axis, with origin at the center of the central icosahedron of the spherical B_{84} unit. The B_{84} unit comprises a central icosahedron (B(5) and B(6)) linked to 12 half-icosahedra of two types. Of the one type, three point in the upward and three in the downward direction; the latter are omitted in the figure. These half-icosahedra involving B(1), B(2) B(9), and B(7) form complete icosahedra by combining with half-icosahedra of the same type in neighboring B_{84} units. The 6 half-icosahedra, involving B(3), B(4), and B(8) atoms, form complete icosahedra by combining with B(10) units (black atoms in the figure). The B_{10} units also link 3 half-icosahedra of the same type from different B_{84} units. The B(15) atom is situated between two B_{10} units. The centers of the three largest holes are marked A(1), D, and E (ref. 3). In ScB_{28}, the A(1) hole is unoccupied; D is occupied by Sc(2) and E by Sc(3). There is another E hole just above the A(1) hole in the figure, and an A(1) hole just above the E hole. The B(16) position (not shown) is situated slightly below the A(1) hole and outside the threefold *c* axis. The S(1) position is occupied by Sc(4).

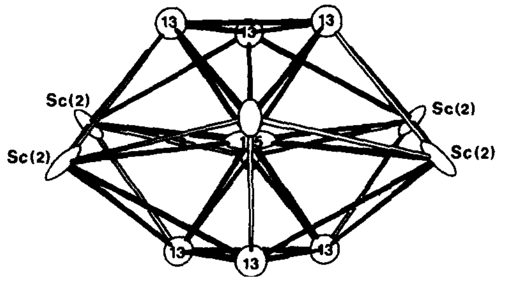

FIG. 2. A perspective view of B(15) and the surrounding B(13) and Sc(2) positions. The *c* axis is vertical in the plane of the paper and passes through B(15). The short Sc(2)–B(13) (2.10 Å) and Sc(2)–Sc(2) (2.49 Å) distances are unfilled. Only nonadjacent Sc(2) positions can be occupied. The thermal ellipsoids are scaled to enclose 70% probability, apart from B(15) whose *c* component is expanded for purposes of clarity.

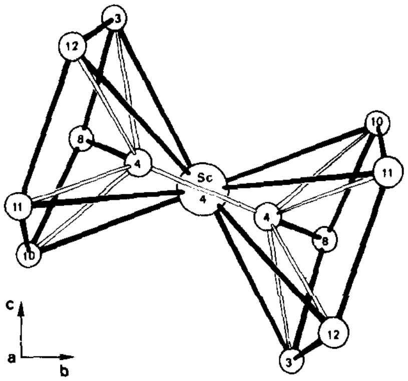

FIG. 3. A perspective view of the Sc(4) environment in the direction of the central icosahedron. The two B(4) atoms are replaced by the scandium atom, which forms a direct connection between two icosahedra.

B(15) are significantly greater in the *xy* plane than in the *c* direction (Table III) and this can be interpreted either in terms of an anisotropic thermal vibration or in terms of an average of a static scattering of the atomic positions. In this case B(15) is probably statically displaced from the mean position by the approximately two Sc(2) atoms. The B(15)–Sc(2) distance is of normal length, 2.46 Å. In other corresponding structures the Me(2)–B(15) distances are relatively longer and no significant anisotropy was found.

The Sc(3) atom occupies to 73% a hole situated on the threefold *c* axis. The environment of the Sc(3) atom is more regular than that of the Sc(2) atom, the distances to the neighboring boron atoms varying between 2.41 and 2.51 Å. The average, 2.46 Å, is very close to the metal–boron radius sum, 2.48 Å. There are no obvious space restrictions on full occupation of the Sc(3) position (see Fig. 1).

The Sc(4) atom occupies a position very close to the center of the line between two B(4) atoms. The Sc(4)–B(4) distance is only 0.86 Å, which excludes the possibility of a simultaneous occupation of the Sc(4) and B(4) positions, so two boron atoms are replaced by one scandium atom at an intermediate position (see Fig. 3).

Since the two B(4) atoms are neighboring atoms in two different isosahedra, the scandium atom forms a direct connection between the two isosahedra. The occupancies of the Sc(4) and B(4) positions are 6 and 92%, respectively. The distances between Sc(4) and its 14 boron neighbors display a large variation, from 2.17 to 2.81 Å. A distance of 2.17 Å is a very short Sc–B distance but no signs of a partial occupation of the B(8) position were found. However, the average of the 14 distances is 2.50 Å, which is close to the radius sum. The Sc(4)–Sc(4) distance of 2.82 Å, which is very short, probably never occurs, since the occupancy of the position is very low (6%).

In other MeB_x structures investigated (*3–5*), the Me(1) position is occupied to a varying extent, from 6 to 72%. This position is located below the Me(3) position on the *c* axis and the metal atom has 12 boron neighbors at the corners of a truncated tetrahedron. The average Me(3)–B distances are all 2.15 or 2.16 Å, but the Sc atom is too large to have 12 boron neighbors at this very short distance. Furthermore, the Sc(1)–Sc(3) distance would be too short (2.4 Å) for simultaneous occupancy.

The scandium occupancy of the three

largest interstitial holes in the β-boron network can be rationalized using space considerations. However, the absence of B(16) and the replacement of two boron atoms by one scandium atom is not readily understood in this manner.

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