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Crystal Structure of α-AlB_{12}

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The crystal structure of α-AlB_{12} (tetragonal; $a = 10.158(2)$ Å, $c = 14.270(5)$ Å, space group $P4_12_12$ or $P4_32_12$) has been determined by the single-crystal X-ray diffraction method. It was solved by the Fourier technique initially based on a partial B_{12} icosahedral structure, which was inferred from crystal chemical considerations. Refinement was made with the aid of a full-matrix least-squares program leading to a final R value of 3.0%. The structure is based on a three-dimensional framework consisting of B_{12} icosahedra, B_{19} units, and single B atoms; the B_{19} unit is a twinned icosahedron with a triangular composition plane and a vacant apex on each side. The chemical unit is $Al_{3.2}\cdot 2B_{12}\cdot B\cdot B_{19}$ and its number in the unit cell is 4. The Al atoms are distributed statistically over five sites in the boron framework. The occupancies of the sites are 72, 49, 24, 15, and 2%, respectively.

Introduction

The basic X-ray crystallographic data for α-AlB_{12} had been reported by Halla and Weil in 1939 (*1*), and were later corroborated by Kohn et al. (*2*) and Matkovich et al. (*3*). Crystals of α-AlB_{12} have tetragonal symmetry with space group $P4_12_12$ or $P4_32_12$ ($a = 10.16$ Å, $c = 14.28$ Å (*2*)), and are sometimes syntaxically intergrown with γ-AlB_{12} (*4*). Kohn and Eckart (*4*), in the study of the geometrical relation between these two phases, suggested that the correct space group for α-AlB_{12} should be $P4_22_12$, rather than $P4_12_12$ (or $P4_32_12$); their analysis was based on the interaction of cell-twinning operators with space group symmetries, and the observed 4_1 or 4_3 symmetry was attributed to a polytypic ordering of identical layers. The structure of α-AlB_{12} is considered to be a B_{12} icosahedral packing structure by analogy with other relevant materials of known structure. The observed density, however, shows that only 14.4 AlB_{12} units can be present in the one unit cell (2), in disagreement with a requirement of the space group observed for this crystal; the space group $P4_12_12$ (or $P4_32_12$) requires the presence of 16 B_{12} units per unit cell. This unreasonable number (14.4), of formula units was interpreted by Lipscomb and Britton (*5*) as due to the partial substitution of B with Al in a B icosahedral or other polyhedral packing structure, whereas Matkovich et al. (*6*) suggested that the structure consists of B_{84} units, because the tetragonal cell size of α-AlB_{12} would accommodate two B_{84} units in accordance with the requirements of the observed density, and because there is no known boride structure composed of defect B_{12} units.

Despite extended efforts, no definite structure of α-AlB_{12} has thus far been obtained. The present authors, therefore, undertook the structure analysis of this crystal by using the X-ray diffraction method. This paper reports the results of the structure analysis and clarifies the correct structure of α-AlB_{12}.

Experimental

Preparation of the Crystals

The single crystals for the structure analysis have been prepared by growth from an aluminium solution. A vertical Al_2O_3 tube furnace

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equipped with an Mo-wire heater and an Al_2O_3 crucible were used. A mixture of 20 g of Al (purity of 99.99%) and 3 g of B (purity of 99.5%) was heated up to 1550°C in an argon atmosphere, kept for 1 hr, and then allowed to cool to room temperature. The crystals grown were separated from the solidified mixture by dissolving excess Al with hydrochloric acid. The separated crystals were examined by X-ray diffraction. The majority of the crystals of α-AlB_{12} obtained were twinned on {101} faces, having plate-like and prismatic forms in which {101} faces do prevail. Crystals free from twinning had the octahedral form enclosed by {101} faces. Systematic absences in the X-ray diffraction patterns, as observed on Weissenberg and precession photographs, indicated the space group for α-AlB_{12} to be either $P4_12_12$ or $P4_32_12$, in agreement with that reported in the literature. The crystal data and the results of chemical analyses are given in Table I. The lattice constants were measured with a diffractometer using 21 general reflections at 22°C. The wavelength used was 1.54184 Å (*7*) for CuKα radiation. The stoichiometry of the crystal was determined by chemical analysis (*8*). Metallic impurities were determined by spectroscopic analysis, and the gaseous impurity, O, was measured by the vacuum fusion technique (*9*).

TABLE I

CRYSTAL DATA AND CHEMICAL ANALYSIS

Symmetry	tetragonal
a (Å)	10.158(2)
c (Å)	14.270(5)
Space group	$P4_12_12$ or $P4_32_12^a$
Chemical unit	$Al_{3.2}\cdot 2B_{12}\cdot B\cdot B_{19}^b$
D_m ($g\cdot cm^{-3}$)	2.55^c
D_x ($g\cdot cm^{-3}$)	2.54
Z	4^d

Al (wt%)	15.96	O (wt%)	0.03
B	83.83	Fe	0.001
Al + B	99.79	Si	0.005
(B/Al)^e	13.1(2)	Mg	0.001

[a] $P4_32_12$ is assumed in this work.

[b] The chemical unit has been established by the present structure analysis.

[c] Pycnometer method.

[d] The chemical unit is twice the asymmetric unit.

[e] Atomic ratio.

Intensity Measurements

The reflections with $0 \leqslant h \leqslant 15, 0 \leqslant k \leqslant 11$, and $0 \leqslant l \leqslant 22$, for which $2\theta < 67°$, were measured by the automatic diffractometer READ-1 (*10*) with Mo$K\alpha$ radiation monochromated with a graphite monochromator. The crystal was approximately octahedral with an average side length of 0.6 mm. It was rotated around the a-axis in the ω-scan mode with a scanning speed of 2°/min. The diffracted X-rays were detected with a scintillation counter with a pulse height analyzer. Strong diffraction beams were attenuated to within the linear range of the counter by using zirconium attenuators. A total of 1478 independent reflections with intensities larger than 2.5 times the standard deviations were collected. These were corrected for Lorentz and polarization effects. No absorption ($\mu R = 0.1$) or extinction corrections were applied.

Structure Determination and Refinement

It was considered that the structure of α-AlB_{12} must, at least in part, be constituted of complete B_{12} icosahedra. Then, a trial partial icosahedral framework model was constructed according to the following considerations. The calculated phases for this model were used for Fourier synthesis to obtain the full structure.

The partial framework, which, as to the number of B atoms, corresponds to about half of the total B in α-AlB_{12}, was constructed according to the space group $P4_32_12$ and in agreement with the requirements of the following crystal chemical assumptions. (1) Every icosahedron is directly linked to neighboring icosahedra approximately along its fivefold axes. (2) There are infinite linear icosahedral chains parallel to the a-axis in which the intericosahedral linkages are affected according to the mode stated above. The first assumption was derived from a common feature of intericosahedral bonds in other relevant crystals and the second from the fact that twice the B_{12}–B_{12} distance in such an icosahedral chain is almost equal to the length of the *a*-axis. All the icosahedra involved in this framework are crystallographically equivalent. The atomic coordinates of the partial structure are presented in Table II. (These agree approximately with those obtained from the final structure refinement.)

A three-dimensional Fourier synthesis, calculated on the basis of the partial structure, gave an extra maximum in addition to those for B sites in the partial framework. The maximum density was about half the density of the B maximum. Assuming this site is fully occupied by Al atoms, a further Fourier synthesis was calculated. The Fourier synthesis thus obtained showed additional 14 maxima with peak values ranging from one-half to one-third of that for the B sites. The assignments of these maxima were made by examining their spatial arrangement; the maxima arranged in the form of a defect icosahedron were assigned as B sites (B(13)–B(22)), and the other four not belonging to the icosahedron as Al sites. All 10 boron sites, B(13)–B(22), were considered to be fully occupied from the almost equal values of their maximum electron densities. Approximate occupancies of the Al sites, including the Al(1) site, were estimated from their relative maximum densities with reference to the total content of Al in the crystal. The atomic coordinates and isotropic temperature factors for B(1)–B(22) and Al atoms were then refined by using the block-diagonal least-squares technique to an *R* value of 4.6%.

TABLE II

The Atomic Coordinates of the Initially Assumed B_{12} Icosahedral Framework ($\times 10^2$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
B(1)	−13	25	12	B(7)	10	21	25
B(2)	−4	13	20	B(8)	11	38	20
B(3)	−4	31	23	B(9)	12	10	16
B(4)	−3	39	12	B(10)	13	20	5
B(5)	−2	12	8	B(11)	13	36	8
B(6)	−1	29	3	B(12)	21	25	16

Further refinement was performed with the aid of a full-matrix least-squares program including occupational parameters of Al sites, resulting in an *R* value of 3.6%. In this case, anisotropic temperature factors were applied to Al(1), Al(2), and Al(3). At this stage, all of the isotropic temperature factors showed reasonable values except for one Al atom, which showed minus values during the refinement. Then this site was reexamined by calculating its distances from surrounding atoms and it was concluded that it was a boron site (B(23)); it was located at distances of 1.79–1.87 Å from four neighboring B atoms, in agreement with twice the atomic radius of B. The full-matrix least-squares refinement of this corrected structure lowered the *R* value to 3.3%. All of the isotropic temperature factors of B atoms including that of B(23) were reasonable, ranging from 0.3 to 0.4 Å^2. However, a difference Fourier synthesis calculated at this stage showed a very small but definite maximum. Considering its distances from neighboring B atoms, which were greater than 2.0 Å, it was assigned as an Al site (Al(5)). A final refinement of 129 independent parameters, including those for the Al(5) site, resulted in an *R* value of 3.0%. The unit weight is given to all reflections. A final difference Fourier synthesis showed no maxima or minima which had a density exceeding 2% of the density of the boron maximum in the Fourier synthesis.

Observed and calculated structure factors are compared in a separate table.[1] The atomic scattering factors for boron and aluminum atoms were taken from the "International Tables for X-ray Crystallography" (*11*). The final atomic coordinates based on the space group $P4_32_12$, temperature factors, and occupancy factors are given in Table III. The calculations for the structure analysis were made by using the program UNICS-II (*12*). The figures of the atomic arrangements were

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[1] See NAPS document No. 02918 for 16 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages. 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE III

FINAL ATOMIC COORDINATES ($\times 10^4$), TEMPERATURE FACTORS, AND OCCUPANCY FACTORS

Atom	Site	x	y	z	B (Å^2)	Atom	Site	x	y	z	B (Å^2
B(1)	8(b)	−1277(2)	2394(2)	1282(1)	0.34(3)	B(15)	8(b)	2038(2)	1968(2)	3452(1)	0.39(2)
B(2)	8(b)	−395(2)	1359(2)	2091(1)	0.36(2)	B(16)	8(b)	4671(2)	1174(2)	4112(1)	0.35(2)
B(3)	8(b)	−455(2)	3119(2)	2317(1)	0.33(2)	B(17)	8(b)	4596(2)	2933(2)	4220(1)	0.36(2)
B(4)	8(b)	−415(2)	3939(2)	1179(1)	0.36(3)	B(18)	8(b)	1856(2)	933(2)	4486(1)	0.39(3)
B(5)	8(b)	−204(2)	1091(2)	808(1)	0.36(2)	B(19)	8(b)	2708(2)	1782(2)	5459(1)	0.35(2)
B(6)	8(b)	−309(2)	2740(2)	296(1)	0.32(2)	B(20)	8(b)	3478(2)	396(2)	4913(1)	0.38(2)
B(7)	8(b)	1073(2)	2231(2)	2456(1)	0.40(2)	B(21)	8(b)	4392(2)	1893(2)	5252(1)	0.38(2)
B(8)	8(b)	1034(2)	3895(2)	1917(1)	0.33(3)	B(22)	4(a)	3317(4)	3317(4)	$\frac{1}{2}$	0.36(4)
B(9)	8(b)	1217(2)	1034(2)	1549(1)	0.34(2)	B(23)	4(a)	354(4)	354(4)	$\frac{1}{2}$	0.35(3)
B(10)	8(b)	1219(2)	1920(2)	447(1)	0.27(2)	Al(1)	8(b)	3021(1)	3688(1)	2589(2)	—[a]
B(11)	8(b)	1137(2)	3628(2)	647(1)	0.31(2)	Al(2)	8(b)	823(1)	118(1)	3086(1)	—[a]
B(12)	8(b)	2054(2)	2596(2)	1391(1)	0.36(3)	Al(3)	8(b)	3130(3)	3932(3)	3419(4)	—[a]
B(13)	8(b)	3140(2)	579(2)	3606(1)	0.36(3)	Al(4)	8(b)	2873(4)	4785(4)	1224(3)	0.37(8)
B(14)	8(b)	3860(2)	2072(2)	3252(1)	0.37(2)	Al(5)	8(b)	3037(35)	3831(43)	2958(91)	0.4(7)

Atom	$B_{11}\cdot 10^5$	$B_{22}\cdot 10^5$	$B_{33}\cdot 10^5$	$B_{12}\cdot 10^5$	$B_{13}\cdot 10^5$	$B_{23}\cdot 10^5$
Al(1)	99(7)	91(7)	84(9)	15(5)	5(4)	10(5)
Al(2)	139(11)	98(11)	104(6)	−13(8)	−31(6)	12(6)
Al(3)	172(24)	81(22)	120(27)	46(17)	16(15)	15(14)

Al(1) : 71.7(7)% Al(2) : 49.1(3)% Al(3) : 24.0(6)% Al(4) : 15.0(3)% Al(5) : 2.1(5)%

[a] Anisotropic temperature factor. The expression of the temperature factor is $\exp\{-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}$.

drawn with the use of program PLOT-60, written by one of the authors (T.S.).

Description of the Structure and Discussion

The crystal structure of α-AlB$_{12}$ is characterized by the presence of a boron framework constituted principally of B$_{12}$ isosahedra and B$_{19}$ units. The B$_{19}$ unit is a twinned icosahedron with two vacant sites, which has never been found in any other compound. The atomic configuration as seen along its twofold axis and one of the edges of the triangular composition plane is shown in Fig. 1. There are 8 B$_{12}$ icosahedra, 4 B$_{19}$ units, 4 single B atoms, and 13.0 Al atoms per unit cell. The Al atoms are distributed statistically over five sites in the boron framework. Figure 2 shows a feature of the arrangement of B$_{12}$ icosahedra as seen along the c-axis. The icosahedra are centered at (0.04, 0.25, 0.13), ii(−0.04, −0.25, 0.63), iii(0.25, 0.54, 0.88), iv(0.75, 0,46, 0.38), v(0.25, 0.04, −0.13), vi(−0.25, −0.04, 0.37), vii(0.46, 0.75, 0.62), and viii(0.54, 0.25, 0.12). Every icosahedron is oriented so that one of its fivefold axes and one of its twofold axes are aligned nearly parallel to the a-axis and c-axis, respectively. It is linked to six neighboring icosahedra by direct intericosahedral B–B bonds. There are four kinds of intericosahedral B–B bonds; B(3)–B(11) around 4_3 screw axes, B(1)–B(12) nearly parallel to the a-axis, and B(10)–B(10) and B(2)–B(2) parallel to (110) or $(1\bar{1}0)$ plane. These bonds are extended approximately normal to the icosahedra. Figure 3 shows the feature of the arrangement of B$_{19}$ units as seen along the c-axis. The centers of the triangular composition planes of these units are located at (−0.26, −0.26, 0), (0.26, 0.26, $\frac{1}{2}$), (0.76, 0.24, $\frac{3}{4}$), and (0.24, 0.76, $\frac{1}{4}$). The twofold axis of every B$_{19}$ unit coincides with that of the crystal. Each B_{19} unit is linked to four neighboring B_{19} units by a direct B–B bond which occurs nearly along a quasi-fivefold axis of the defect icosahedron constituting one side of the B_{19} unit. All of the B–B bonds between B_{19} units are equivalent to one another and nearly parallel to a {100} plane. Every B_{12} icosahedron is surrounded by six B_{12} icosahedra, five B_{19} units, and a single B atom. So, each of the 11 apex atoms of the icosahedron is bonded to an apex atom of a next B_{12} or B_{19} unit, and the remaining one is linked to the single B atom. Every B_{19} unit is surrounded by 10 B_{12} icosahedra, 4 B_{19} units, and a single B atom. Each of 14 apex atoms of the B_{19} units is bonded to an apex atom of a next B_{12} or B_{19} unit, and two apex atoms are bonded to the single atom. The remaining three B atoms are those located at the apexes of the triangular composition plane; none of them are bonded to the boron atoms outside of the B_{19} unit. Figure 4 shows a feature of the linkages between B_{12} icosahedra and B_{19} units. It is projected on the (102) plane along the [101]-axis. Every direct B–B bond between

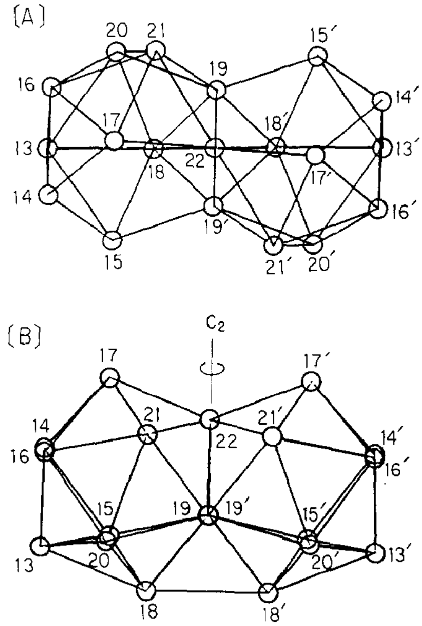

FIG. 1. Atomic arrangement of the B_{19} unit, as seen along the twofold axis (A) and along the edge of the triangular composition plane which is perpendicular to the twofold axis (B).

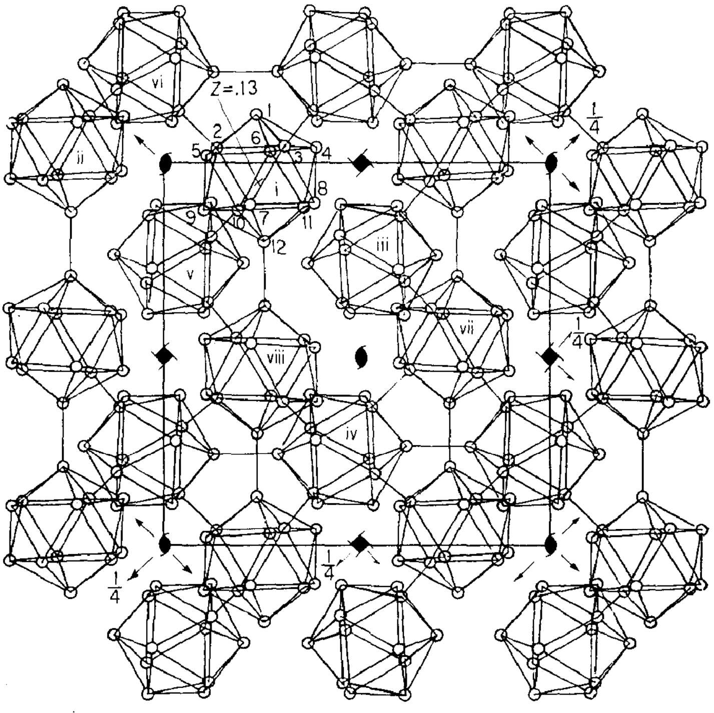

FIG. 2. B_{12} icosahedral arrangement as seen along the c-axis. Icosahedra are marked with the symmetry codes: i(x, y, z), ii$(-x, -y, \frac{1}{2}+z)$, iii$(\frac{1}{2}-y, \frac{1}{2}+x, \frac{3}{4}+z)$, iv$(\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{4}+z)$, v$(y, x, -z)$, vi$(-y, -x, \frac{1}{2}-z)$, vii$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{4}-z)$, viii$(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}-z)$.

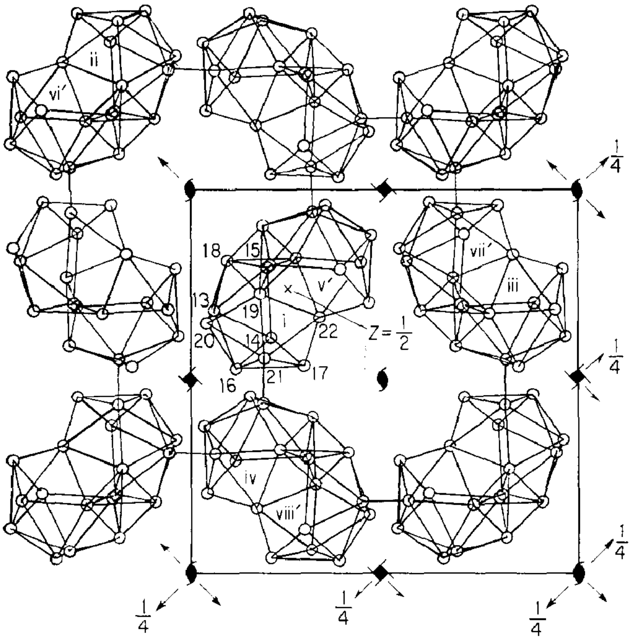

FIG. 3. Arrangement of B_{19} units as seen along the c-axis. Defect icosahedra involved in B_{19} units are marked with following symmetry codes, where i, ii, iii, and iv are identical with those used in Fig. 2: i, ii, iii, iv, v′(y, x, $1-z$), vi′($-y$, $-x$, $\frac{3}{2}-z$), vii′($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{7}{4}-z$), viii′($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{5}{4}-z$).

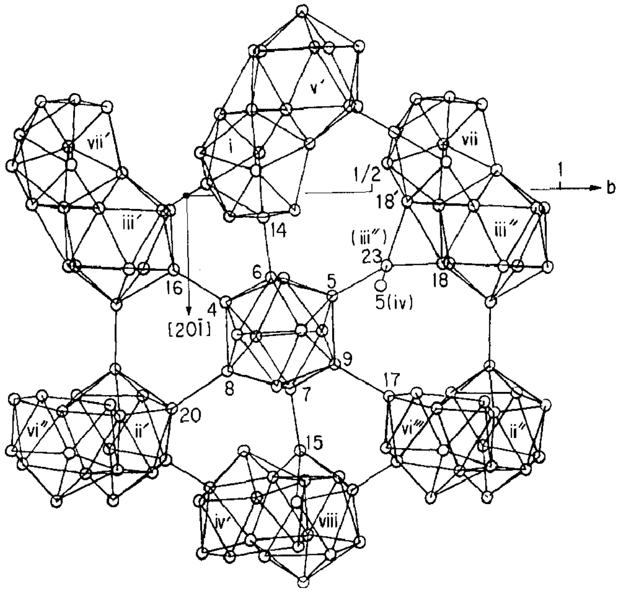

FIG. 4. The nature of the linkages between B_{12} icosahedron and B_{19} units as projected on the (102) plane along the [101]-axis. The icosahedron, defect icosahedra involved in B_{19} units and the B atoms, B(23) and B(5), are marked with following symmetry codes, where i, iv, vii and viii and v′ are identical to those used in Figs. 2 and 3, respectively: i, ii′($1-x$, $-y$, $-\frac{1}{2}+z$), ii″($1-x$, $1-y$, $-\frac{1}{2}+z$), iii′($\frac{1}{2}-y$, $-\frac{1}{2}+x$, $-\frac{1}{4}+z$), iii″($\frac{1}{2}-y$, $\frac{1}{2}+x$, $-\frac{1}{4}+z$), iv, iv′($\frac{1}{2}+y$, $\frac{1}{2}-x$, $-\frac{3}{4}+z$), v′, vi″($1-y$, $-x$, $\frac{1}{2}-z$), vi‴($1-y$, $1-x$, $\frac{1}{2}-z$), vii, vii″($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{4}-z$), viii.

B_{12} and B_{19} units occurs nearly along an icosahedral fivefold axis and a quasi-fivefold axis of the defect icosahedron involved in the B_{19} unit. There are five kinds of direct B_{12}–B_{19} linkages and one kind of indirect linkage in which a single B atom functions to join a B_{19} unit and two B_{12} icosahedra together. The mode of the linkage through the intermediary B atom is illustrated in more detail in Fig. 5, which is projected on the (001) plane along the *c*-axis; the single B atom is linked to none of the B atoms except the four indicated in the figure.

Interatomic distances in α-AlB_{12} are presented in Table IV. The intraicosahedral and intericosahedral B–B bond distances range from 1.736(3) to 1.858(3) Å and from 1.626(3) to 1.812(3) Å, respectively. Their respective mean values are 1.805(3) and 1.709(3) Å, which agree well with the values of 1.810(3) and 1.709(6) Å observed for these bond types in AlB_{10} (*13*). On the other hand, the variations in the B–B bond distances in both bond types are rather significant as compared with those observed in AlB_{10} (1.783(5)–1.839(6) Å for intraicosahedral bonds, and 1.629(7)–1.786(6) Å for intericosahedral bonds). The angles of the triangles of the icosahedra range from 57.0(1)–62.0(1)°. As in the case of the bond lengths, the variation in the angles is a little greater than that observed in AlB_{10} (58.3(2)–60.8(2)°). The bonds connecting boron atoms within a B_{19} unit (except for one of exceptional length) range in length from 1.738(3) to 1.907(3) Å with a mean value of 1.814(3) Å. The bond of unusual length (1.979(3) Å) is between two atoms, each of which belongs to a different side of the B_{19} unit (B(18)–B(18) in Fig. 1 or Fig. 5). Including this bond, the average bond length is 1.820(3) Å. The angles of the triangles of the defect icosahedron involved in the B_{19} unit range from 57.0(1) to 63.3(1)°. The length of the B–B bond connecting B_{19} units is 1.715(3) Å and the bonds connecting B_{12} and B_{19} units by direct contact range in length from 1.662(3) to 1.868(3) Å with a mean value of 1.745(3) Å. On the whole, the external direct bonds between the boron units, B_{12}–B_{12}, B_{19}–B_{19}, and B_{12}–B_{19}, tend to have shorter bond lengths as compared with the bonds within these units. The bond lengths between the single B atom and two B atoms each of which belongs to neighboring B_{12} and B_{19} units are 1.874(4) and 1.794(4) Å, respectively.

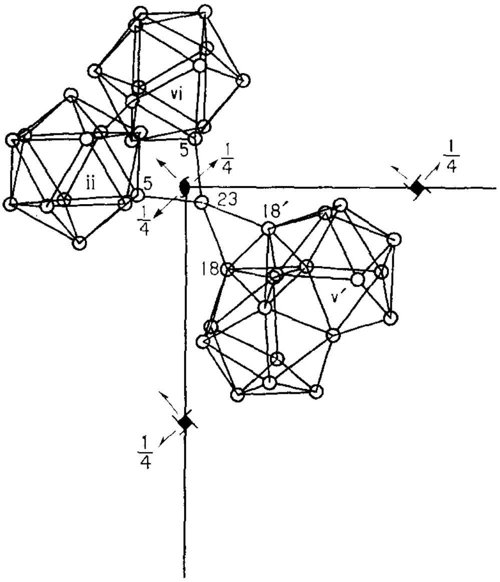

FIG. 5. The nature of the linkage between a B_{12} icosahedron and a B_{19} unit through an intermediary single B atom as seen along the *c*-axis. These units are marked with the symmetry codes which are identical to those used in Figs. 2 and 3.

The distribution of Al sites in the boron framework, as seen along the *c*-axis, is presented in Fig. 6, where B_{12} icosahedra and B_{19} units are depicted with solid and dotted lines, respectively. The Al(5) site, located between the Al(1) and Al(3) sites, is omitted in this figure. The variations of the distances of B neighbors from the Al sites are demonstrated graphically in Fig. 7, where the first neighbors are distinguishable from the second neighbors. The Al sites are surrounded by 11, 13, 10, 15, and 16 first neighbors and are occupied up to 71.7(7)%, 49.1(3)%, 24.0(6)%, 15.0(3)% and 2.1(5)%, respectively. Figure 8 shows perspective drawings illustrating the coordinations of the Al sites. The shortest distances for Al(1, 3, 5)–B, 2.079(2), 2.043(4), and 2.02(5) Å, are somewhat shorter than the sum of the covalent Al and the average B radius, 1.26 (*14*) and 0.87 Å (*15*). The B atoms situated at such short intervals from Al sites are those be-

TABLE IV

INTERATOMIC DISTANCES (Å)

B–B bond length within B_{12} iscsahedron

B(1)–B(2)	1.802(3)	B(2)–B(9)	1.842(3)	B(5)–B(9)	1.791(3)	B(8)–B(11)	1.837(3)
–B(3)	1.851(3)	B(3)–B(4)	1.826(3)	–B(10)	1.751(3)	–B(12)	1.839(3)
–B(4)	1.804(3)	–B(7)	1.807(3)	B(6)–B(10)	1.775(3)	B(9)–B(10)	1.813(3)
–B(5)	1.844(3)	–B(8)	1.799(3)	–B(11)	1.796(3)	–B(12)	1.815(3)
–B(6)	1.754(3)	B(4)–B(6)	1.758(3)	B(7)–B(8)	1.858(3)	B(10)–B(11)	1.761(3)
B(2)–B(3)	1.819(3)	–B(8)	1.811(3)	–B(9)	1.783(3)	–B(12)	1.736(3)
–B(5)	1.863(3)	–B(11)	1.779(3)	–B(12)	1.855(3)	B(11)–B(12)	1.760(3)
–B(7)	1.812(3)	B(5)–B(6)	1.831(3)				

B–B bond lengths within B_{19} unit

B(13)–B(14)	1.759(3)	B(14)–B(17)	1.799(3)	B(17)–B(21)	1.825(3)	B(19)–B(19)	1.868(3)
–B(15)	1.814(3)	B(15)–B(18)	1.823(3)	–B(22)	1.756(4)	–B(20)	1.791(3)
–B(16)	1.819(3)	–B(19)	1.748(3)	B(18)–B(18)	1.979(3)	–B(21)	1.740(3)
–B(18)	1.847(3)	B(16)–B(17)	1.796(3)	–B(19)	1.807(3)	–B(22)	1.801(4)
–B(20)	1.907(3)	–B(20)	1.844(3)	–B(19)	1.851(3)	B(20)–B(21)	1.847(3)
B(14)–B(15)	1.875(3)	–B(21)	1.807(3)	–B(20)	1.840(3)	B(21)–B(22)	1.848(3)
–B(16)	1.738(3)						

B–B bond lengths in the linkages B_{12}–B_{12}, B_{19}–B_{19}, B_{12}–B_{19}, and B_{12}–B–B_{19}

B(1)–B(12)	1.713(3)	B(10)–B(10)	1.626(3)	B(6)–B(15)	1.730(3)	B(9)–B(17)	1.715(3)
B(2)–B(2)	1.812(3)	B(13)–B(21)	1.715(3)	B(7)–B(15)	1.748(3)	B(23)–B(5)	1.874(4)
B(3)–B(11)	1.686(3)	B(4)–B(16)	1.662(3)	B(8)–B(20)	1.868(3)	B(23)–B(18)	1.792(4)

Al–B and Al–Al distances[a]

Al(1)–B(14)	2.079(2)	Al(2)–B(18)	2.406(2)	Al(4)–B(8)	2.300(4)	Al(5)–B(6)	2.56(7)
–B(5)	2.223(2)	–B(9)	2.418(2)	–B(15)	2.328(4)	–B(17)	2.57(10)
–B(8)	2.246(2)	–B(21)	2.481(2)	–B(1)	2.377(4)	–B(7)	2.67(5)
–B(12)	2.263(3)	–B(5)	2.507(2)	–B(12)	2.387(4)	–B(12)	2.75(11)
–B(6)	2.299(2)	–B(13)	2.512(2)	–B(2)	2.410(4)	–B(19)	2.84(11)
–B(20)	2.309(2)	B(3)–B(14)	2.043(4)	–B(19)	2.414(2)	–B(1)	2.86(11)
–B(1)	2.355(2)	–B(18)	2.114(4)	–B(20)	2.462(4)	–B(21)	2.87(12)
–B(15)	2.361(2)	–B(17)	2.135(5)	–B(2)	2.467(4)	–B(22)	2.98(13)
–B(18)	2.363(2)	–B(13)	2.220(4)	–B(23)	2.627(4)	Al(1)–Al(3)	1.216(6)
–B(23)	2.368(3)	–B(15)	2.284(4)	–B(18)	2.662(4)	Al(4)	2.250(4)
–B(7)	2.479(2)	–B(21)	2.325(6)	–B(18)	2.823(4)	Al(5)	0.55(13)
Al(2)–B(22)	2.194(4)	–B(22)	2.351(6)	Al(5)–B(14)	2.02(5)	Al(2)–Al(2)	2.151(2)
–B(2)	2.249(2)	–B(19)	2.448(5)	–B(18)	2.14(4)	–Al(3)	2.146(5)
–B(2)	2.267(2)	–B(23)	2.486(5)	–B(15)	2.26(6)	–Al(4)	2.472(4)
–B(17)	2.277(2)	–B(20)	2.509(4)	–B(20)	2.28(5)	–Al(5)	2.72(10)
–B(15)	2.309(2)	Al(4)–B(7)	2.238(4)	–B(23)	2.34(5)	Al(3)–Al(5)	0.67(13)
–B(7)	2.342(2)	–B(5)	2.249(6)	–B(8)	2.52(8)	Al(4)–Al(5)	2.66(12)
–B(9)	2.381(2)	–B(3)	2.262(4)	–B(13)	2.52(8)		
–B(17)	2.384(2)	–B(11)	2.274(4)	–B(5)	2.54(10)		

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[a] For Al–B distances, those between Al sites and their respective B first neighbors are listed. For Al–Al distances, those shorter than 2.8 Å are listed.

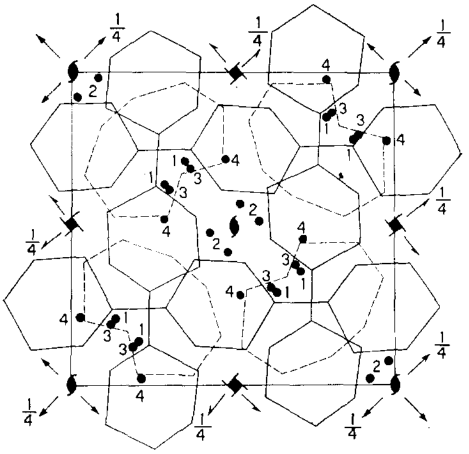

FIG. 6. The nature of the distribution of Al sites in the boron framework as seen along the c-axis. B_{12} icosahedra and B_{19} units are depicted with solid and dotted lines, respectively. The Al(5) site is omitted in the figure; it is situated between Al(1) and Al(3) sites.

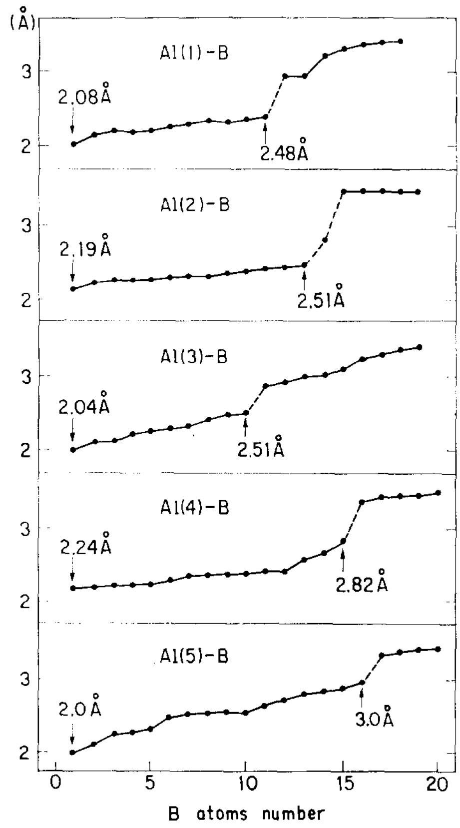

FIG. 7. Variations in the distances of surrounding B atoms from Al sites.

longing to the B_{19} unit. The distances between metal sites, Al(1)–Al(3, 4, 5), Al(2)–Al(2, 3), and Al(3)–Al(5), are considerably shorter than the covalent radius sum, 2.52 Å (Table IV). However, since the sum of the occupancies of the two or three sites, situated at the short interval, is in every case less than 100%, it is possible that the Al atoms distribute statistically over the sites in the whole crystal without any abnormal contact. Considering that Al atoms can be present in α-AlB_{12} with an atomic radius of 1.173 Å (the minimum Al–B distance in α-AlB_{12} minus the average B radius), the Al(2)–Al(4) distance, 2.472(4) Å, probably allows the simultaneous occupation of both sites. It is of interest to note that in the triplet of Al(1)–Al(5)–Al(3) (Fig. 9A) one site is almost always occupied and the remaining two are empty, because the sum of the occupancies of these sites is 98% and none of the simultaneous occupations are permited owing to the unusually short intervals between these sites (Table IV). A similar situation is also present concerning the doublet of Al(2)–Al(2) (Fig. 9B), since twice the occupancy of this site is 98% and the very short interval (Table IV) prohibits simultaneous occupation. Therefore, in this doublet, one site is almost always occupied and the other empty.

The chemical composition determined by the occupational refinement is $AlB_{13.6\pm0.2}$, which is almost equal to that determined within the experimental error of the chemical analysis (Table I). This fact, together with the reasonable values of isotropic temperature factors and interatomic distances, proves the validity of the assignments of the atomic sites in this crystal. Therefore, the partial substitution of Al for B, as suggested by Lipscomb and Britton (*5*) (see the Introduction), almost never take place. The value, 14.4 formula units per cell, reported in the earlier work (*2*), has been considered to be unreasonable because, by analogy with other relevant crystals with B_{12} icosahedral structures, α-AlB_{12} has been regarded as a B_{12} icosahedral compound and the space group requires the presence of 16 B_{12} icosahedra per unit cell. This apparent contradiction is resolved in this work through the confirmation of the presence of the new B_{19} unit. The

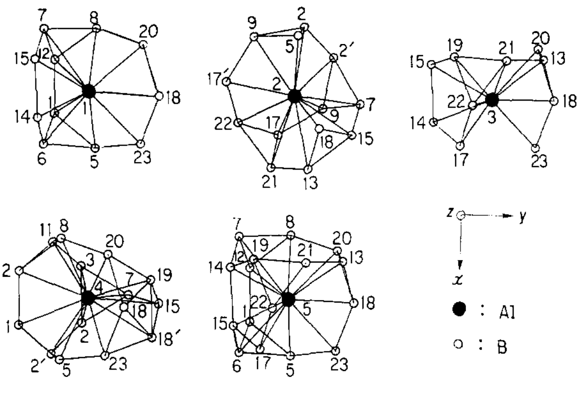

FIG. 8. Perspective drawings illustrating the coordinations of Al sites.

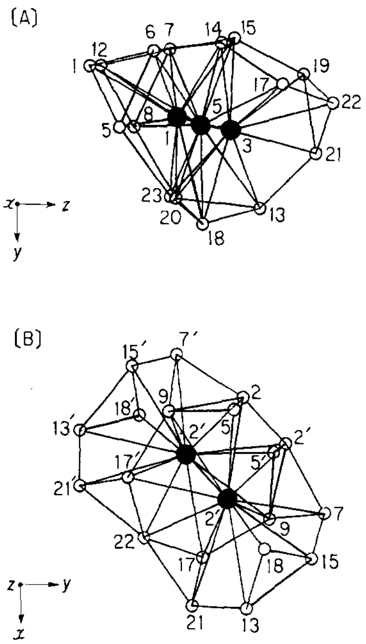

FIG. 9. Al(1)–Al(5)–Al(3) triplet (A) and Al(2)–Al(2) doublet (B) with their B first neighbors. One position of this triplet or doublet is almost always occupied and the remaining two (or one) are empty. See text.

formula unit and its number in the unit cell, determined in this work, are $Al_{3.2}\cdot 2B_{12}\cdot B\cdot B_{19}$ (or $AlB_{13.6}$) and 4 (or 12.9), respectively. The density calculated from these data and the cell volume is 2.54 g/cm^3, which is almost equal to the observed density (Table I). The chemical composition observed for the present crystal is slightly different from $AlB_{12.2}$, observed for the α-AlB_{12} phase by Matkovich et al. *(3)*. As the occupancy of the Al(4) site in this phase can be increased a certain extent without any abnormal contact between the metal atoms, such a small variation in the chemical composition may practically occur according to crystal growth conditions; as for the growth temperature, the present crystal has been grown by cooling the Al–B melt from 1550°C, while Matkovich et al. *(3)* obtained their crystal by cooling the melt from 1700°C.

In addition to the presence of the B_{19} units, the structure of α-AlB_{12} is unusual in that the single B atom site, as well as every B site in the B_{12} and B_{19} units, is fully occupied, unlike most of the other B_{12} icosahedral metal borides such as AlB_{10}, $C_8Al_{2.1}B_{51}$ *(16)* or C_4AlB_{24} *(17)*, and YB_{66} *(18)*. The B_{12} icosahedra, B_{19} units, and single B atoms, being present in a ratio of 2 : 1 : 1, are linked in a striking and neat way; all of the B–B linkages between these units are accomplished approximately along the fivefold axis of the icosahedra or the similar direction in the defect icosahedra involved in the B_{19} units, making up an infinite three-dimensional framework. The Al atoms must necessarily function to nucleate and to stabilize the complex boron framework, since α-AlB_{12} is formed at about 1000°C from the elemental mixture and is stable up to about 2000°C *(19)*. As Hoard and Hughes pointed out *(20)*, the higher beryllium boride, BeB_6 (tetragonal; $a = 10.16$ Å, $c = 14.28$ Å, space group $P4_12_12$ or $P4_32_12$) *(21)*, possibly involves the same boron framework as in α-AlB_{12}. Therefore, the structure of BeB_6 may be determinable easily by the use of

Fourier methods applied to the boron framework of α-AlB_{12}.

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