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Metal Distributions in $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$ of α-AlB_{12} Structure Type

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Distributions of metals in $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$ were investigated by X-ray diffraction using four different crystals. The boron frameworks of the crystals are almost the same as that in α-AlB_{12}. However, the metal distributions are considerably different from that in α-AlB_{12}; Al atoms occupy only Al(1, 2, 3) sites with a great increment in occupancy of Al(3), leaving the other two, Al(4, 5), almost empty; on the other hand, Be atoms partially occupy two to five sites that are vacant in the case of α-AlB_{12}. Significant differences in the Be distributions are also found among the four $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$ crystals. However, in every case, including α-AlB_{12}, the metallic valence electron numbers, allotted to the B_{12} and B_{20} units in proportion to the frequencies in the contacts of the units with the metals, are ~2 and ~5.5, respectively. It is inferred that the variations in the metal distributions, primarily caused by the difference in the atomic sizes of Al and Be, arise, so as to preserve a negative charge balance between B_{12} and B_{20}; a ratio of about 1 : 3 should presumably be essential to the stabilization of α-AlB_{12} structure type compounds.

Introduction

Recently, the author has determined the crystal structure of an aluminum beryllium boride having an approximate composition, $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$, by X-ray diffraction.[1] The boron framework of this substance was almost the same as that of α-AlB_{12} (*1*, *2*). However, there was a significant difference between the metal distributions. In the present work, therefore, structures of three different crystals, giving chemical compositions and crystal data similar to those for $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$, were analyzed using much more intensity data, in order to examine the nature of the metal distribution in the boron framework. This paper reports the results of the structure analysis and the examination, suggesting a common rule concerning metal distributions in α-AlB_{12} structure type compounds.

The crystals were prepared by growth from aluminum solutions. Two crystals of the present three were of the same batch from which the previous crystal (distorted octahedron, hereafter called crystal I) had been selected; one was a rather massive plate-like crystal (crystal II) and the other a very thin platelet (crystal III), having well-developed {101} faces. A coarse comparison of each of the two intensity sets obtained from crystal II and crystal III with the data observed for crystal I showed that almost certainly their structures were the same. However, separate structure refinements revealed that there was an essential difference in the beryllium distribution between the previous crystal and the present two crystals; on the other hand, there was no marked difference between crystal II and crystal III. The third of the present specimens, crystal IV, was prepared under different growth conditions.

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[1] Proceedings, 6th International Symposium on Boron and Borides, Druzhba-Varna, Bulgaria, 1978 (Special Issue of *J. Less Common Metals*), submitted for publication.

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Experimental

Preparation of the Crystals

A vertical Al_2O_3 tube furnace equipped with a Mo wire heater and Al_2O_3 crucibles were used. The temperature of the furnace was controlled by an automatic voltage regulator and measured with an optical pyrometer. Purities of the starting materials were 99.99, 99.5, and 99.5% for Al, Be, and B, respectively.

Crystals I, II, and III. A mixture of 20 g Al, 0.1 g Be, and 1.0 g B was heated in an argon atmosphere at 1400°C for 1 hr and then allowed to cool to room temperature. The reaction mixture was treated with hydrochloric acid, dissolving excess Al. The insoluble product, which was a mixture of red crystals and black crystals, was examined by X-ray diffraction; red crystals showed the same space group and almost the same cell dimensions as α-AlB_{12}; black crystals gave the same crystal data as α-tetragonal boron (*3*). (Seemingly, the red crystals are the same phase as a mixed crystal of α-AlB_{12} and BeB_6 (*4, 5*), and the black ones $AlBeB_{24}$ (*5, 6*).)

Crystal IV. A mixture of 100 g Al, 0.5 g Be, and 5 g B was heated in an argon atmosphere up to 1500°C, kept for 1 hr, and then allowed to cool to room temperature. Both red crystals and black crystals were obtained from the reaction mixture. The red crystals were mostly massive and much larger as compared with the former, so the specimen for the intensity measurements was selected from the fragments obtained by crushing large distorted octahedral crystals.

Intensity Measurements

The intensity data were collected on a Rigaku–Denki four-circle X-ray diffractometer with monochromatic Mo$K\alpha$ radiation. A 2θ–θ scan mode at a rate of 2° (in θ)/min was used. The background counts of 10 sec were measured on each side of the scanning width, which was monotonically increased by θ according to $\Delta\theta = 1 + 0.5 \tan \theta$. In order to check the stabilities of the diffractometer and crystal setting, three standard reflections were examined after each of all 100 reflections had been measured; these showed no noticeable variation during the measurement. The intensities were corrected for Lorentz and polarization effects. No absorptions or extinction corrections were made. Independent reflections with structure factors larger than 2.5 times the standard deviations were collected by averaging the F_o's for equivalent reflections.

Separate data for the intensity measurements are presented in Table I together with the crystal data and the results of the chemical analysis. Lattice constants were determined with a diffractometer using 20–25 general reflections. The densities were measured by the gradient tube technique (*7*) using tetrabromoethane and acetone. The metal contents were determined by wet chemical analysis (*8*) and the impurities by emission spectroscopic analysis.

Refinement of the Structures

The structures of the present crystals were refined starting from the structure of crystal I, which had been solved applying the Fourier method to the boron framework of α-AlB_{12} and refined to an R value of 5.6%. Therefore, brief descriptions of the structures of these crystals will be given here to facilitate discussions. The boron framework of α-AlB_{12} is constituted by a B_{12} icosahedron (B(1–12)), a B_{19} unit (B(13–22)), and a single B atom (B(23)); the B_{19} unit is a twinned icosahedron with a triangular composition plane and a vacant apex on each side; $13.0Al \cdot 8B_{12} \cdot 4B \cdot 4B_{19}$ are contained in the tetragonal unit cell ($a = 10.158(2)$ Å, $c = 14.270(5)$ Å, space group $P4_12_12$ or $P4_32_12$). All the linkages between these boron units are affected along the pseudo-fivefold axes of the icosahedra or defect icosahedra involved in the B_{19} units. The Al

TABLE I

CRYSTAL AND INTENSITY MEASUREMENT DATA, AND CHEMICAL ANALYSIS

Crystal	II	III	IV
Space group	$P4_12_12$ or $P4_32_12$	$P4_12_12$ or $P4_32_12$	$P4_12_12$ or $P4_32_12$
a (Å)	10.171(3)[a]	10.168(4)[b]	10.174(1)[a]
c (Å)	14.238(4)	14.262(1)	14.235(6)
V (Å^3)	1473	1475	1473
Formula unit[c]	$Al_{1.1}Be_{0.7}B_{22}$	$Al_{1.1}Be_{0.8}B_{22}$	$Al_{1.2}Be_{0.5}B_{22}$
D_m (g cm^{-1})	2.5	2.5	2.5
D_x (g cm^{-1})	2.47	2.47	2.48
Z	8	8	8
μ for Mo$K\alpha$ (cm^{-1})	2.2	2.2	2.4
Crystal dimensions (mm)	0.6 × 0.4 × 0.2	0.3 × 0.3 × 0.05	0.8 × 0.8 × 0.4
Reflections measured	$0 \leq h \leq 18$	$0 \leq h \leq 18$	$0 \leq h \leq 18$
	$0 \leq k \leq 18$	$0 \leq k \leq 18$	$0 \leq k \leq 18$
	$0 \leq l \leq 25$	$0 \leq l \leq 25$	$0 \leq l \leq 24$
$2\theta_{max}$ (°)	78	80	78
Number of reflections collected	2369	2253	2442

Crystal	II, III	IV
Al (wt%)	10.0	10.4
Be	2.7	2.3
Fe	0.08	0.01
Cu	0.01	0.0001
Mg		0.04
B	Balance	Balance
(Composition)	($Al_{1.0}Be_{0.8}B_{22}$)	($Al_{1.1}Be_{0.7}B_{22}$)

[a] $\lambda(MoK\alpha_1) = 0.70926$ Å.

[b] $\lambda(MoK\alpha) = 0.71069$ Å.

[c] Asymmetric unit determined by the structure analysis.

atoms are distributed among five sites (Al(1–5)) with varing occupancies. The boron framework of crystal I ($a = 10.180(2)$ Å, $c = 14.257(2)$ Å, space group $P4_12_12$ or $P4_32_12$) is almost the same as that of α-AlB_{12}, but there is a significant difference in the metal distribution; Al atoms occupy only three sites (Al(1, 2, 3)), leaving the other two (Al(4, 5)) empty; on the other hand, Be atoms are accommodated in the two truncated tetrahedral holes that are vacant in the case of α-AlB_{12}.

Refinements of the structures of the present crystals were performed by the block-diagonal least-squares method. Anisotropic temperature factors were applied to the Al(1, 2, 3) sites, and the unit weight was given to all the reflections. The atomic scattering factors were those given in the International Tables for X-Ray Crystallography (1974) (*9*). All the calculations were made by the program UNICS-III (*10*) on the FACOM 230-75 computer of this Institute.

Crystal II

Starting from the final parameters of crystal I, a preliminary refinement of the structure was made; the R value obtained was 4.0%. A difference synthesis calculated at this stage showed two additional maxima with densities of 1.5 and 0.8 e Å^{-3}. The greater maximum was located in the vicinity of the vacant apex of B_{19} unit. The distances of five apex atoms of the open pentagonal face of the B_{19} unit from this site ranged from 1.91 to 2.01 Å, in agreement with the Be–B distances observed for BeB_3 by Mattes *et al.* (*11*). Therefore it was assigned as a Be site (B(3)). The other maximum was situated at the center of a truncated tetrahedral hole that was just the same size as those accommodating Be(1) and Be(2) atoms. Thus it was assigned as a Be site (Be(4)). The final refinement of 135 independent parameters was performed including the occupancies of Be(3) and Be(4) sites fixing the temperature factors for these sites at 0.5 Å^2; the *R* value obtained was 3.3%. The final difference Fourier map showed no maxima exceeding 0.5 e Å^{-3}.

Crystal III

Refinement of the structure, starting from the final parameters of crystal I, gave an *R* value of 5.9%. The difference Fourier map obtained at this stage indicated the presence of the Be(3) (1.5 e Å^{-3}) and Be(4) (0.8 e Å^{-3}) atoms. Refinements including those for the occupancies of Be(3) and Be(4) resulted in an *R* value of 5.6%. Yet, the subsequent difference Fourier map showed extra two maxima with a density of 0.7 e Å^{-3}. One was situated at the center of a truncated tetrahedral hole having the same size as the other similar holes accommodating Be atoms. Consequently, it was assigned as a Be site (Be(5)). The other was situated at the center of an intericosahedral B–B bond. So, this maximum was considered to be a chance superposition of a random noise and a difference electron density of the intericosahedral two-centered bond, which had been found to attain 0.45 e Å^{-3} (on an average 0.2 e Å^{-3}) (*12*). Further refinement of 139 independent parameters was performed including occupancy of the Be(5) site fixing the temperature factors for Be(3, 4, 5) sites at 0.5 Å^2; the *R* value obtained was 5.5%. The final difference Fourier map showed no maxima exceeding 0.5 e Å^{-3} except that (0.7 e Å^{-3}) mentioned above.

Crystal IV

The preliminary refinement similar to those for the former gave an *R* value of 2.9%. The subsequent difference Fourier synthesis showed small but definite maxima at Al(5) and Be(3) sites (0.7 e Å^{-3}). Adding these metal sites, the final refinement of 135 independent parameters was performed fixing the temperature factors for the two sites at 0.5 Å^2; the *R* value obtained was 2.6%. The final difference Fourier map indicated no maxima greater than 0.45 e Å^{-3}.

Results and Discussion

Description of the Metal Distributions

The final atomic coordinates based on the space group $P4_32_12$ and temperature factors, and interatomic distances for crystal III are shown in Tables II and III, respectively. The corresponding data for crystal II (Tables IV and V) and crystal IV (Tables VI and VII), and the observed and calculated structure factors for crystals II, III, and IV (Tables VIII, IX, and X), are presented separately.[2]

So far as the boron frameworks are concerned, the structures of the aluminum beryllium borides are essentially the same as that of α-AlB_{12}; the average B–B bond

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[2] See NAPS document No. 03519 for 85 pages of supplementary material. 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 $21.25. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.00 for a fiche.

TABLE II

Final Atomic Coordinates ($\times10^4$) and Temperature Factors of Crystal-III

Atom	Site	x	y	z	B (Å^2)	Atom	Site	x	y	z	B (Å^2)
B(1)	8(*b*)	−1270(2)	2369(2)	1275(2)	0.33(2)	B(17)	8(*b*)	4611(2)	2937(2)	4220(2)	0.33(2)
B(2)	8(*b*)	−389(2)	1339(2)	2100(2)	0.34(2)	B(18)	8(*b*)	1861(2)	943(2)	4494(2)	0.47(2)
B(3)	8(*b*)	−429(2)	3109(2)	2311(2)	0.32(2)	B(19)	8(*b*)	2717(2)	1785(2)	5460(2)	0.31(2)
B(4)	8(*b*)	−389(2)	3934(2)	1179(2)	0.33(2)	B(20)	8(*b*)	3489(2)	400(2)	4930(2)	0.35(2)
B(5)	8(*b*)	−230(2)	1072(2)	804(2)	0.35(2)	B(21)	8(*b*)	4402(2)	1916(2)	5252(2)	0.34(2)
B(6)	8(*b*)	−318(2)	2725(2)	298(2)	0.35(2)	B(22)	4(*a*)	3350(4)	3350(4)	$\frac{1}{2}$	0.35(3)
B(7)	8(*b*)	1094(2)	2241(2)	2464(2)	0.35(2)	B(23)	4(*a*)	355(4)	355(4)	$\frac{1}{2}$	0.43(3)
B(8)	8(*b*)	1063(2)	3913(2)	1926(2)	0.32(2)	Al(1)	8(*b*)	3036(2)	3717(2)	2599(2)	—[a]
B(9)	8(*b*)	1197(2)	1047(2)	1555(2)	0.35(2)	Al(2)	8(*b*)	760(2)	146(2)	3187(2)	—[a]
B(10)	8(*b*)	1198(2)	1918(2)	458(2)	0.32(2)	Al(3)	8(*b*)	3130(2)	3938(2)	3360(2)	—[a]
B(11)	8(*b*)	1154(2)	3641(2)	649(2)	0.29(2)	Be(1)	8(*b*)	2839(8)	914(8)	769(5)	0.5(1)
B(12)	8(*b*)	2057(2)	2615(2)	1400(2)	0.31(2)	Be(2)	4(*a*)	2791(15)	2791(15)	0	0.4(4)
B(13)	8(*b*)	3124(2)	589(2)	3621(2)	0.42(2)	Be(3)	8(*b*)	2915(15)	3703(14)	3713(10)	0.5
B(14)	8(*b*)	3853(2)	2081(2)	3254(2)	0.38(2)	Be(4)	8(*b*)	4866(150)	512(150)	2691(100)	0.5
B(15)	8(*b*)	2050(2)	1993(2)	3444(2)	0.37(2)	Be(5)	8(*b*)	2980(58)	1310(56)	2154(40)	0.5
B(16)	8(*b*)	4659(2)	1168(2)	4118(2)	0.38(2)						

Atom	$B_{11}\times10^5$	$B_{22}\times10^5$	$B_{33}\times10^5$	$B_{12}\times10^5$	$B_{13}\times10^5$	$B_{23}\times10^5$
Al(1)	106(14)	99(14)	118(8)	24(10)	19(8)	26(8)
Al(2)	109(18)	82(17)	129(10)	−4(12)	−51(10)	−16(10)
Al(3)	228(19)	95(15)	185(10)	62(13)	0(11)	1(10)

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

TABLE III

INTERATOMIC DISTANCES IN CRYSTAL III (Å)

B–B bond lengths within B_{12} icosahedron

B(1)–B(2)	1.812(3)	B(2)–B(9)	1.815(3)	B(5)–B(9)	1.803(3)	B(8)–B(11)	1.845(3)
–B(3)	1.865(3)	B(3)–B(4)	1.820(3)	–B(10)	1.758(3)	–B(12)	1.824(3)
–B(4)	1.831(3)	–B(7)	1.796(3)	B(6)–B(10)	1.761(3)	B(9)–B(10)	1.797(3)
–B(5)	1.819(3)	–B(8)	1.808(3)	–B(11)	1.832(3)	–B(12)	1.832(3)
–B(6)	1.735(3)	B(4)–B(6)	1.759(3)	B(7)–B(8)	1.865(3)	B(10)–B(11)	1.774(3)
B(2)–B(3)	1.826(3)	–B(8)	1.821(3)	–B(9)	1.780(3)	–B(12)	1.751(3)
–B(5)	1.874(3)	–B(11)	1.766(3)	–B(12)	1.846(3)	B(11)–B(12)	1.754(3)
–B(7)	1.840(3)	B(5)–B(6)	1.832(3)				

B–B bond lengths within B_{19} unit

B(13)–B(14)	1.767(3)	B(14)–B(17)	1.803(3)	B(17)–B(21)	1.815(3)	B(19)–B(19)	1.875(3)
–B(15)	1.814(3)	B(15)–B(18)	1.849(3)	–B(22)	1.749(3)	–B(20)	1.781(3)
–B(16)	1.812(3)	–B(19)	1.748(3)	B(18)–B(18)	1.955(3)	–B(21)	1.744(3)
–B(18)	1.825(3)	B(16)–B(17)	1.806(3)	–B(19)	1.806(3)	–B(22)	1.837(3)
–B(20)	1.913(3)	–B(20)	1.834(3)	–B(19)	1.840(3)	B(20)–B(21)	1.857(3)
B(14)–B(15)	1.855(3)	–B(21)	1.806(3)	–B(20)	1.852(3)	B(21)–B(22)	1.844(4)
–B(16)	1.748(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)	1.719(3)	B(10)–B(10)	1.668(3)	B(6)–B(14)	1.732(3)	B(9)–B(17)	1.721(3)
B(2)–B(2)	1.780(3)	B(13)–B(21)	1.730(3)	B(7)–B(15)	1.721(3)	B(23)–B(5)	1.854(4)
B(3)–B(11)	1.698(3)	B(4)–B(16)	1.689(3)	B(8)–B(20)	1.827(3)	B(23)–B(18)	1.796(5)

Metal–B and metal–metal distances[a]

Al(1)–B(14)	2.081(3)	Al(3)–B(14)	2.032(3)	Be(2)–2B(3)	2.05(3)	Be(5)–B(12)	1.95(6)
–B(5)	2.194(3)	–B(18)	2.101(3)	–2B(11)	2.09(3)	–B(14)	1.97(6)
–B(8)	2.232(3)	–B(17)	2.192(3)	–2B(2)	2.13(3)	–B(6)	1.99(6)
–B(12)	2.274(3)	–B(13)	2.234(3)	–2B(12)	2.14(3)	–B(9)	2.02(6)
B(6)	2.297(3)	–B(15)	2.266(3)	Be(3)–B(22)	1.92(1)	–B(1)	2.03(6)
–B(20)	2.309(3)	–B(21)	2.380(3)	–B(19)	1.93(1)	–B(16)	2.04(6)
–B(18)	2.339(3)	–B(22)	2.424(3)	–B(21)	1.93(1)	–B(4)	2.05(6)
–B(23)	2.339(3)	–B(23)	2.440(3)	–B(15)	1.99(1)	–B(17)	2.06(6)
–B(15)	2.352(3)	–B(20)	2.488(3)	–B(14)	2.02(1)	–B(21)	2.12(6)
–B(1)	2.357(3)	–B(19)	2.499(3)	–B(17)	2.03(1)	–B(15)	2.18(6)
–B(7)	2.488(3)	Be(1)–B(4)	1.973(8)	–B(13)	2.20(1)	–B(7)	2.19(6)
Al(2)–B(2)	2.187(3)	–B(6)	1.974(8)	Be(4)–B(6)	1.9(1)	–B(13)	2.22(6)
–B(22)	2.262(3)	–B(10)	2.006(8)	–B(4)	2.0(1)	Al(1)–Al(3)	1.114(3)
–B(17)	2.282(3)	–B(10)	2.006(8)	–B(11)	2.0(1)	Al(2)–Al(3)	2.151(3)
–B(2)	2.289(3)	–B(9)	2.015(8)	–B(16)	2.0(1)	–Al(2)	2.353(4)
–B(9)	2.319(3)	–B(16)	2.029(8)	–B(3)	2.1(1)	Al(1)–Be(3)	1.59(1)
–B(15)	2.320(3)	–B(17)	2.054(8)	–B(4)	2.1(1)	–Be(5)	2.53(6)
–B(18)	2.321(3)	–B(1)	2.071(8)	–B(8)	2.1(1)	Al(2)–Be(3)	2.17(1)
–B(5)	2.355(3)	–B(14)	2.098(8)	–B(14)	2.1(1)	Al(3)–B(3)	0.60(1)
–B(7)	2.391(3)	–B(12)	2.106(8)	–B(20)	2.1(1)	Be(1)–Be(2)	2.20(3)
–B(13)	2.523(3)	–B(3)	2.184(8)	–B(21)	2.1(1)	–Be(4)	2.2(1)
–B(17)	2.536(3)	–B(11)	2.194(8)	–B(13)	2.2(2)	–Be(5)	2.02(6)
–B(9)	2.541(3)	Be(2)–2B(10)	1.96(3)	–B(16)	2.2(2)	Be(4)–Be(5)	2.2(1)
–B(21)	2.558(3)	–2B(1)	2.00(3)				

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[a] For metal–B distances, those between metal sites and their respective B first neighbors are listed. For metal–metal distances, those shorter than 2.9 Å are listed.

lengths within B_{12} and B_{19} units (Table XI) agree well with the values observed for α-AlB_{12}, 1.805(3) and 1.820(3) Å (*1*). However, when each of the B–B bond lengths in the present crystals is compared with its equivalent in α-AlB_{12}, some of them show much larger variations than their standard deviations. The extents of the shifts in B–B bond lengths from the corresponding B–B bond lengths of α-AlB_{12} are outlined in Table XI. There are no noticeable variations in the equivalent B–B bond lengths among aluminum beryllium borides.

In Table XII, the occupancies of the metal sites are compared with those observed for crystal I and α-AlB_{12}. Using the same reflections as in the previous work, the occupational parameters for the crystal I were reexamined by the BDLS program fixing the temperature factors for Be(1) and Be(2) sites at 0.5 $Å^{-2}$ ($R = 4.1\%$). This value was considered to be reasonable, since the refinements for the present three crystals, using much more intensity data (Table I), resulted in temperature factors around 0.5 $Å^2$ for the same sites; the previous structure analysis, based on 1108 reflections, had given much larger temperature factors, 1.7 $Å^2$ for Be(1) and 6 $Å^2$ for Be(2). Therefore, the data for crystal I in Table XII are somewhat changed from those obtained in the previous work. In comparison with the case of α-AlB_{12}, the most unusual features of the Al distribution in the aluminum beryllium borides are that the occupancy of Al(3) site is greatly increased and the incorporation of Al into the Al(4) site never takes place. The Be atoms occupy smaller holes as compared with those accommodating Al atoms (see metal–boron distances in Table III); these holes are empty in the case of α-AlB_{12}. No marked difference in the Al distribution is seen among aluminum beryllium borides except that, in the case of crystal IV, the occupancy of the Al(3) site is much more increased and there may be a slight occupation of the Al(5) site. An essential difference among the aluminum beryllium borides is concerned with the occupation of the vacant apical site (Be(3)) of the B_{19} unit by Be atoms; it is remarkable in the case of crystals II and III, but it never occurs in crystal I and scarcely in crystal IV. A slight occupation of the Be(4) site takes place in crystals II and III, and that of the Be(5) site is noticed only in the latter. The occupancies of the two sites might appear too small to regard the sites as real. Yet, each of the sites, as in the cases of Be(1) and Be(2) sites, lies just in the center of a truncated tetrahedral hole,

TABLE XI

AVERAGE B–B BOND LENGTHS WITHIN B_{12} AND B_{19} UNITS, AND SHIFTS IN B–B BOND LENGTHS FROM THE EQUIVALENTS IN α-AlB_{12} (Å)

Crystal		II	III	IV
Average B–B bond lengths within units[a]	B_{12}	1.806(2)	1.808(3)	1.806(2)
	B_{19}	1.821(2)	1.821(3)	1.820(2)
Shifts in B–B bond lengths within units[b]	B_{12}	−0.029 ~ +0.033	−0.027 ~ +0.036	−0.024 ~ +0.030
	B_{19}	−0.031 ~ +0.032	−0.024 ~ +0.036	−0.036 ~ +0.025
Shifts in B–B bond lengths in linkages[b]	B_{12}–B_{12}	−0.023 ~ +0.045	−0.032 ~ +0.042	−0.019 ~ +0.041
	B_{12}–B_{19}	−0.040 ~ +0.008	−0.041 ~ +0.027	−0.033 ~ +0.021
	B_{19}–B_{19}	+0.012	+0.015	+0.011
	B_{12}–B(23)	−0.023	−0.020	−0.018
	B_{19}–B(23)	+0.005	+0.004	+0.013

[a] The average lengths within B_{12} and B_{19} of crystal I are 1.809(7) and 1.823(7) (Å), respectively.

[b] The shifts in similar lengths are observed for crystal I.

TABLE XII

COMPARISONS BETWEEN OCCUPANCIES OF METAL SITES IN $Al_{\sim 1.1}Be_{\sim 0.6}B_{22}$ AND α-AlB_{12}

Metal	Site	Crystal I	Crystal II	Crystal III	Crystal IV	α-AlB_{12}
Al(1)	8(*b*)	0.388(5)	0.375(2)	0.377(4)	0.390(2)	0.717(7)
Al(2)	8(*b*)	0.325(5)	0.316(3)	0.317(4)	0.341(2)	0.491(3)
Al(3)	8(*b*)	0.438(5)	0.395(3)	0.378(5)	0.477(2)	0.240(6)
Al(4)	8(*b*)					0.150(3)
Al(5)	8(*b*)				0.021(1)	0.021(5)
Be(1)	8(*b*)	0.38(1)	0.37(1)	0.38(2)	0.33(1)	
Be(2)	4(*a*)	0.19(2)	0.19(1)	0.19(2)	0.19(1)	
Be(3)	8(*b*)		0.17(1)	0.19(1)	0.05(1)	
Be(4)	8(*b*)		0.05(1)	0.03(1)		
Be(5)	8(*b*)			0.06(1)		

being surrounded by 12 B atoms with Be–B distances similar to those for Be(1)–12B and Be(2)–12B (Table III). There might be some interrelation between the nature of the Be distribution and crystal shapes, since the crystals with a considerable amount of Be atoms on vacant apexes of B_{19} units, crystals II and III, are plate-like crystals and the others distorted octahedra.

Figures 1 and 2 show the natures of the coordinations of Be atoms. As seen from Fig. 1a, the truncated tetrahedral hole filled with a Be(2) atom lies on the twofold axis, sharing two hexagonal faces with the adjacent two equivalent truncated tetrahedral holes that are occupied by a Be(1) atom. The two truncated tetrahedral holes that accommodate Be(4) and Be(5) also share a hexagonal face (Fig. 1b). The Be(5) hole is linked to the Be(1) hole sharing a hexagonal face that is approximately parallel to the (001) plane. All these sites are enclosed tetrahedrally with four B–B–B triangular faces, each of which belongs to a separate B_{12} or B_{19} unit. The Be(3) atom is located so as to cap the open pentagonal face of the B_{19} unit (Fig. 2).

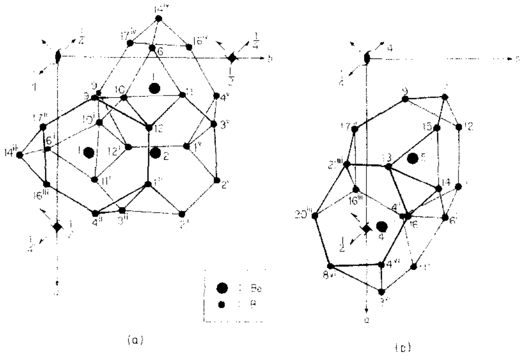

FIG. 1. The nature of the coordinations of Be(1, 2, 4, 5) atoms as seen along the c-axis. Each of the atoms is enclosed tetrahedrally with B–B–B triangular planes. The Be and B atoms are designated by the following symmetry codes: none (x, y, z), i $(y, x, -z)$, ii $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}-z)$, iii $(\frac{1}{2}-y, -\frac{1}{2}+x, -\frac{1}{4}+z)$, iv $(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}-z)$, v $(\frac{1}{2}-y, \frac{1}{2}+x, -\frac{1}{4}+z)$, vi $(1-y, -x, \frac{1}{2}-z)$.

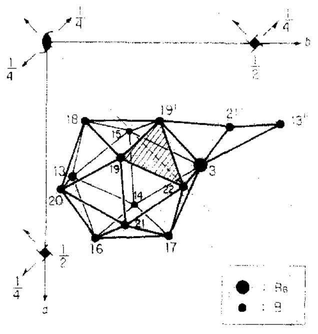

FIG. 2. The nature of the coordinations of the Be(3) atoms as seen along the c-axis. The hatched triangular section is the composition plane of the B_{19} unit. The Be and B atoms are designated by the following symmetry codes: none (x, y, z), i $(y, x, 1-z)$, ii $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{4}-z)$.

The distances between the Be(3) site and the five boron atoms of the pentagonal face range from 1.92(1) to 2.02(1) Å, which are appreciably larger than the B–B bond lengths, 1.745(3)–1.913(3) Å, within the defect icosahedron involved in the B_{19} unit. As indicated in Fig. 2, the Be(3) atom is also in contact with two additional boron atoms, one of which belongs to the same B_{19} unit capped by the Be atom and the other to a neighboring B_{19} unit; the distance from Be(3) to the former is 1.92(1) Å and to the latter, 2.20(1) Å (Table III).

Charge Balance between B_{12} and B_{20}

In a recent work on the valence electron distribution in the boron structure of α-AlB_{12}, Ito *et al.* (*12*) pointed out that from an electronic point of view $B \cdot B_{19}$ can be regarded as a chemical unit, B_{20}. They also suggested that to attain a stable electronic configuration the B_{20} unit needs more negative charge than the B_{12} icosahedron; according to their preliminary molecular orbital calculations, the ionic formula $\frac{10}{3}Al^{+3} \cdot 2B_{12}{}^{-2} \cdot B_{20}{}^{-6}$ may be given to α-AlB_{12}. The actual electron transfer from Al to the boron framework should, as they noted, be much smaller presumably due to back-transfer. Yet, from the results of the following examination, the formula seems to be helpful in understanding the stability of the unusual α-AlB_{12} structure.

In this examination, all the valence electrons of the metals are assumed to be equivalent with respect to the role in stabilizing the boron framework. Then, Z/n valence electrons may be allotted to every metal–boron contact, where Z and n are the number of the valence electrons and the coordination number of the metal, respectively. The sum of the Z/n values over all the boron atoms within the B_{12} or B_{20} unit and over all the metals concerned is the total number of the valence electrons of the unit. Thus, if the ionic formula $\frac{10}{3}Al^{+3} \cdot 2B_{12}{}^{-2} \cdot B_{20}{}^{-6}$ has some chemical significance, the sums of the Z/n values for B_{12} and B_{20} in α-AlB_{12} structure type compounds should be around 2 and 6, respectively.

The results of the examination are summarized in Table XIII, where the sums of Z/n values for B_{12} and B_{20} units are presented for each crystal together with the data from which the final sums are derived. The numbers of the valence electrons are 3 and 2 for Al and Be, respectively. Every metal atom except Al(5) is regarded as being in contact with its respective B first neighbors (*1*). As for the Al(5)–B contacts, because of the wide variances in the distances from the metal site to surrounding B atoms (*1*), 10 B situated within 2.6 Å from the site are taken into account. n_1 and n_2 are the numbers of the coordinations of the B of B_{12} and the B of B_{19} about the metal site, respectively, and n is the total coordination number, $n = n_1 + n_2$. The frequency of the metal–B_{12} contact, f_1, is obtained by multiplying n_1 by the metal occupancy, p. As for the metal–B_{20} contacts, the frequency, f_2, is twice the value $n_2 \times p$, because the B_{20} unit lies on the twofold axis of the crystal (*1*) and the metal sites except Be(2) atoms are located at the general positions. f_1 for Be(2)–B_{12} contacts is $\frac{1}{2}(n_1 \times p)$, because the metal atom lies on the twofold axis. $(f_1 \times Z)/n$ or $(f_2 \times Z)/n$ is the number of the valence electrons allotted to the B_{12} or B_{20} unit in proportion to the frequencies of the contacts with the metals in each site.

In the case of α-AlB_{12}, the sums of the Z/n values for the B_{12} and B_{20} units are 2.2 and 5.3, respectively. As for the aluminum beryllium borides, the summations of Z/n's resulted in values similar to those obtained for α-AlB_{12}; 1.9 and 5.2 for crystal I, 1.9 and 5.6 for crystal II, 1.9 and 5.7 for crystal III, and 1.8 and 5.5 for crystal IV. Considering the significant differences in the metal distributions, the approximate agreement between the values for α-AlB_{12} and the ternary borides is noteworthy. Furthermore, the sums of the Z/n values, ~2 and ~5.5,

TABLE XIII

NUMBERS OF METALLIC VALENCE ELECTRONS ALLOTTED TO B_{12} AND B_{20} PROPORTIONATELY WITH THE FREQUENCY OF CONTACT OF THE UNITS WITH METALS

				Coordination number ($n = n_1 + n_2$)		Frequency of metal–unit contact			
Crystal	Metal	Site	Occupancy	M–B(1–12) n_1	M–B(13–23) n_2	M–B(B_{12}) f_1	M–B(B_{20}) f_2	$\frac{f_1 \times Z}{n}$ (B_{12})	$\frac{f_2 \times Z}{n}$ (B_{20})
α–AlB_{12}	Al(1)	8(*b*)	0.72	6	5	4.32	7.20	1.18	1.97
	Al(2)	8(*b*)	0.49	6	7	2.94	2.51	0.68	1.58
	Al(3)	8(*b*)	0.24	0	10	0	4.80	0	1.44
	Al(4)	8(*b*)	0.15	9	3	1.35	0.90	0.34	0.24
	Al(5)	8(*b*)	0.02	3	7	0.06	0.28	0.02	0.08
								Sum: 2.2	5.3
I	Al(1)	8(*b*)	0.39	6	5	2.34	3.90	0.64	1.06
	Al(2)	8(*b*)	0.33	6	7	1.98	4.62	0.46	1.07
	Al(3)	8(*b*)	0.44	0	10	0	8.80	0	2.64
	Be(1)	8(*b*)	0.38	9	3	3.42	2.28	0.57	0.38
	Be(2)	4(*a*)	0.19	12	0	1.14	0	0.19	0
								Sum: 1.9	5.2

II	Al(1)	8(*b*)	0.38	6	5	2.88	3.80	0.62	1.04
	Al(2)	8(*b*)	0.32	6	7	1.92	4.48	0.44	1.03
	Al(3)	8(*b*)	0.40	0	10	0	8.00	0	2.40
	Be(1)	8(*b*)	0.37	9	3	3.33	2.22	0.56	0.37
	Be(2)	4(*a*)	0.19	12	0	1.14	0	0.19	0
	Be(3)	8(*b*)	0.17	0	7	0	2.38	0	0.68
	Be(4)	8(*b*)	0.05	6	6	0.30	0.60	0.05	0.10
								Sum: 1.9	5.6
III	Al(1)	8(*b*)	0.38	6	5	2.28	3.80	0.62	1.06
	Al(2)	8(*b*)	0.32	6	7	1.92	4.48	0.44	1.03
	Al(3)	8(*b*)	0.38	0	10	0	7.60	0	2.28
	Be(1)	8(*b*)	0.38	9	3	3.42	2.28	0.57	0.38
	Be(2)	4(*a*)	0.19	12	0	1.14	0	0.19	0
	Be(3)	8(*b*)	0.19	0	7	0	2.66	0	0.76
	Be(4)	8(*b*)	0.03	6	6	0.18	0.36	0.03	0.06
	Be(5)	8(*b*)	0.06	6	6	0.36	0.72	0.06	0.12
								Sum: 1.9	5.7
IV	Al(1)	8(*b*)	0.39	6	5	2.34	3.90	0.64	1.06
	Al(2)	8(*b*)	0.34	6	7	2.04	4.76	0.47	1.10
	Al(3)	8(*b*)	0.48	0	10	0	9.60	0	2.88
	Al(5)	8(*b*)	0.02	3	7	0.06	0.28	0.02	0.08
	Be(1)	8(*b*)	0.33	9	3	2.97	1.98	0.50	0.33
	Be(2)	4(*a*)	0.18	12	0	1.08	0	0.18	0
	Be(3)	8(*b*)	0.02	0	7	0	0.28	0	0.08
								Sum: 1.8	5.5

observed for the five crystals, are all compatible with the charge assignment, $\frac{10}{3}Al^{+3}\cdot 2B_{12}^{-2}\cdot B_{20}^{-6}$. This means that the varying metal distributions in these compounds have a common feature with respect to the stabilization of the boron framework, suggesting some validity of the ionic formula. As seen from Table III, the distances of the coordinations of B about Be are, in general, appreciably shorter than those of the coordinations of B about Al. Therefore, the variations of the metal distributions are considered to arise from the differences of the component metals without markedly changing a charge balance of about 1 : 3 between the B_{12} and B_{20} units. Preservation of the charge balance, possibly essential to make up the stable boron framework, may be attained by modulating occupancies of metal sites; in the case of the aluminum beryllium borides, the increment of the frequencies in the metal–B_{12} contact, caused by the incorporation of Be(1) and Be(2) atoms, is practically compensated for by the increase in the occupancy of the Al(3) site which is coordinated with the B atoms of only the B_{20} (B(13–23)) units (Table III).

The present treatment is qualitative in nature, and might be crude in that the frequency in the contacts of boron units with metals is averaged over the whole crystal and variances in the metal–B distances are disregarded. Yet, the results obtained may shed some light on the understanding of the formation of α-AlB_{12} structure type compounds.

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