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The α-AlB_{12} Structure

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The crystal structure of α-AlB_{12}, reported recently by Higashi, Sakurai, and Atoda is confirmed by an independent investigation of a different crystal. The space group is $P4_12_12$ (or $P4_32_12$) and our lattice parameters are $a = 10.161(7)$ Å, $c = 14.283(8)$ Å. The structure was partially solved by Patterson methods, when the full structure was communicated to us by Higashi *et al.* Utilizing 2393 reflections, our structure refinement yields an R value of 2.6% with very low standard deviations for structural parameters (0.0001 for atomic coordinates of boron atoms). Within the standard deviations there is excellent agreement with all parameters determined by Higashi *et al.* It is found, nevertheless, that the structural parameters of α-AlB_{12} do not serve to account for the reported Debye–Scherrer patterns of "BeB_6," "LiB_6," or β-tetragonal boron, all of which have the same cell dimensions and space group as α-AlB_{12}.

Introduction

The elusive problem of the structure of α-AlB_{12} has been solved finally by Higashi *et al.* (*1*). We had been seriously engaged with this problem for about a year when we learned of their results just as we were approaching the final solution ourselves. The structural information made available to us allowed us to achieve readily a highly refined solution using our more extensive data on a different crystal. In the main, we confirm to a remarkable degree the structure found by Higashi, *et al.* (*1*).

There are three main components of the structure of α-AlB_{12}: (1) a linear array of B_{12} icosahedra, a feature found in other higher borides; (2) a novel configuration of 19 boron atoms formed by face sharing of two incomplete icosahedra, each lacking one apical boron; (3) an unusual statistical distribution of Al among four or possibly five sites. We had already ascertained the presence of the chains of icosahedra and most of the Al positions. In the completion of our structure refinement, we thought it quite likely that we would find differences in the location and distribution of Al sites for our crystal, and possibly in the B_{19} boron configuration. It is surprising to us that the result is such an excellent detailed agreement in all respects with the reported structure (*1*). We believe it worthwhile to document our confirmatory findings because of the importance of this structure to the crystal chemistry of higher borides, especially since it contains highly unusual features such as the statistical distribution of Al atoms and the novel B_{19} configuration. Also, our more extensive data set results in lower standard deviations for the structural parameters and the interatomic distances.

Experimental

The crystal used for our investigation was prepared in the following manner.[1] The

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[1] This preparation was made by G. Sturgeon *et al.* (*10*) during a general study of the crystal growth of rare earth borides utilizing molten aluminum as a flux.

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elements, α-rhombohedral boron[2] and aluminum, as powders, were placed in an alumina crucible under an inert atmosphere. The crucible, in a tantalum jacket, was heated under purified argon by means of induction heating. The temperature was raised gradually over a period of 30 min from ambient to 1500°C. The specimen was held at 1500°C for 15 min, then allowed to cool gradually to less than 1000°C, and finally quenched. An especially well-formed crystal of dimensions 0.40 × 0.35 × 0.30 mm was selected for X-ray intensity measurements. Its density was determined by flotation in bromoform to be 2.65 ± 0.08 g/cm^3. Lattice parameters were $a = 10.161(7)$ Å, $c = 14.283(8)$ Å, and the space group was $P4_12_12$ or $P4_32_12$.

X-Ray diffraction intensities were measured with a three-circle automated diffractometer in the θ–2θ scan mode using monochromatic Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). A total of 3843 independent reflections ($\theta_{max} = 45°$) were scanned of which 2393 with intensity $> 2\sigma$ were used in the structural analysis. Lorentz-polarization corrections were made, but none for absorption.

Structure Determination and Refinement

Our initial attempts to interpret the Patterson maps as well as the use of direct methods (MULTAN) were unsuccessful, but the occurrence of the chains of icosahedra were noted to be compatible with the Patterson maps. The origin location proved to be a problem restricting further progress. Subsequent proper choice of the origin resulted in an electron density map which indicated locations of most of the aluminum positions and some of the nonicosahedral boron atoms. It was at this point that we obtained the structural information from Higashi *et al.* (*1*). The procedure, then, utilizing their boron parameters, was essentially one of refinement. We were cautious regarding the aluminum positions and used initially only Al(1), Al(2), and Al(3) which were clearly indicated on our first Fourier plots. Subsequent Fourier and difference Fourier plots called for Al(4) and ultimately Al(5). We were not inclined to accept Al(5) with its 2% occupancy as real but the Fourier based on a least-squares refinement to an $R = 3\%$ with its exclusion showed significant electron density at the position designated as Al(5) by Higashi *et al.* (*1*). The ultimate least-squares refinement with $R = 2.6\%$ indicated the occupancy to be 2.0(5)%. The final difference Fourier map showed no maxima greater than 2% of that for a boron peak. Our structural parameters and interatomic distances are given in Tables I and II, respectively, in the same format (for $P4_32_12$) as used by Higashi *et al.* (*1*). The high quality of the data, especially for boron atoms, is indicated by the very small and constant standard deviations (0.0001 for the coordinates, and 0.01 Å for B, except for two cases). The overall agreement with the Higashi *et al.* data is most striking—in no case are the differences outside the limits indicated by the standard deviations. The largest difference concerns the occupancy factor for Al(1) where the difference is 3σ. It is clear, then, that the structure is indeed well established. Higashi *et al.* (*1*) describe and illustrate this structure in great detail quite adequately and we have no reason to say more about the formal description.

The table of structure factors is on deposit and is available upon request.[3]

Discussion and Interpretation

There is no readily apparent rationale for the structure of α-AlB_{12} in terms of existing knowledge of the crystal chemistry of higher borides. Only one feature, namely the icosahedral arrangement, is recognizable as a characteristic of higher boride structures. Each of the boron atoms within the icosahedral units fulfills the criterion, often stated

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[2] α-Rhombohedral boron was prepared by the hydrogen reduction, at 800°C, of a carefully purified boron(III) bromide according to a technique which has been described elsewhere (see, for example, (*2*), (*3*), or (*4*).

[3] See NAPS document No. 02960 for 5 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th St., New York, NY 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 I

ATOMIC COORDINATES (× 10^4), TEMPERATURE FACTORS, AND OCCUPANCY FACTORS

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
B(1)	−1281(1)	2397(1)	1281(1)	0.27(1)	B(15)	2037(1)	1966(1)	3451(1)	0.33(1)
B(2)	−398(1)	1360(1)	2092(1)	0.30(1)	B(16)	4671(1)	1178(1)	4113(1)	0.30(1)
B(3)	−455(1)	3118(1)	2315(1)	0.29(1)	B(17)	4594(1)	2930(1)	4220(1)	0.33(1)
B(4)	−415(1)	3937(1)	1179(1)	0.29(1)	B(18)	1861(1)	933(1)	4486(1)	0.38(1)
B(5)	−203(1)	1090(1)	810(1)	0.31(1)	B(19)	2705(1)	1779(1)	5457(1)	0.32(1)
B(6)	−308(1)	2740(1)	297(1)	0.26(1)	B(20)	3479(1)	395(1)	4911(1)	0.34(1)
B(7)	1075(1)	2232(1)	2454(1)	0.30(1)	B(21)	4392(1)	1893(1)	5249(1)	0.33(1)
B(8)	1030(1)	3894(1)	1916(1)	0.30(1)	B(22)	3315(1)	3315(1)	1/2	0.32(2)
B(9)	1215(1)	1036(1)	1547(1)	0.29(1)	B(23)	356(1)	356(1)	1/2	0.33(2)
B(10)	1210(1)	1920(1)	447(1)	0.26(1)	Al(1)	3022(1)	3689(1)	2588(1)	—[a]
B(11)	1137(1)	3628(1)	648(1)	0.29(1)	Al(2)	823(1)	117(1)	3030(1)	—[a]
B(12)	2048(1)	2597(1)	1391(1)	0.29(1)	Al(3)	3134(2)	3932(2)	3428(2)	—[a]
B(13)	3140(1)	575(1)	3606(1)	0.34(1)	Al(4)	2873(3)	4784(3)	1227(2)	—[a]
B(14)	3857(1)	2071(1)	3255(1)	0.32(1)	Al(5)	3080(24)	3817(24)	2986(20)	0.3(2)

	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
Al(1)	114(4)	98(4)	97(2)	22(3)	−7(3)	−15(2)
Al(2)	125(7)	76(6)	109(3)	−18(5)	41(4)	−18(4)
Al(3)	184(15)	81(13)	146(8)	58(11)	−5(9)	−26(8)
Al(4)	106(19)	101(19)	48(8)	14(15)	6(10)	−18(11)

Al(1) 75.3(5)%	Al(2) 48.8(4)%	Al(3) 24.6(4)%	Al(4) 16.2(4)%	Al(5) 2.0(4)%

[a] Anisotropic temperature factors. The expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

as the Hoard–Hughes postulate (*5*), that it occurs as the apex of a pentagonal pyramid with respect to other icosahedral borons and forms a sixth bond approximately along a pseudo fivefold axis of the icosahedron. This postulate is satisfied by some of the boron atoms in the incomplete icosadra of the B$_{19}$ unit, but this unit is novel among boride structures and is not easily interpretable by existing bonding theories.

Equally difficult to understand is the nature of the aluminum distribution. Both the sites for Al(1) and Al(3) are separately satisfactory for fully accommodating aluminum atoms and it is strange that a preference exists to the extent of three to one in favor of Al(1). The 50% occupancy of Al(2) sites is reasonable, but the 15 to 16% occupancy of Al(4) is another puzzle. Then, of course, the small occupancy (2%) of Al(5) is quite unusual. It cannot be strongly claimed that indeed aluminum atoms and not boron atoms occupy these sites. Related to the problem of the distribution of aluminum atoms is the important question of why the preferred stoichiometry is AlB$_{13.2}$.

We consider the several unusual features of the α-AlB$_{12}$ structure, which we are presently unable to explain, to constitute an important challenge to the theorist and the crystal chemist who can be assured that the structure is very well established.

It has been expected that the knowledge of the structure of α-AlB$_{12}$ would be important in shedding light on several related structures that have the same cell dimensions and the same space group. These are "BeB$_6$" (*6*), "LiB$_6$" (*7*, *8*), and β-tetragonal boron (*9*). A not unreasonable hope is that the reported polycrystalline diffraction patterns would suffice for deducing the similarities and differences in structure for these other substances.

TABLE II

INTERATOMIC DISTANCES (Å)

B–B Bond lengths within a B_{12} icosahedron

B(1)–B(2)	1.804(2)	B(2)–B(9)	1.844(2)	B(5)–B(9)	1.785(2)	B(8)–B(11)	1.835(2)
–B(3)	1.850(2)	B(3)–B(4)	1.824(2)	–B(10)	1.752(2)	–B(12)	1.836(2)
–B(4)	1.802(2)	–B(7)	1.809(2)	B(6)–B(10)	1.775(2)	B(9)–B(10)	1.809(2)
–B(5)	1.847(2)	–B(8)	1.796(2)	–B(11)	1.795(2)	–B(12)	1.812(2)
–B(6)	1.753(2)	B(4)–B(6)	1.755(2)	B(7)–B(8)	1.856(2)	B(10)–B(11)	1.762(2)
B(2)–B(3)	1.816(2)	–B(8)	1.807(2)	–B(9)	1.782(2)	–B(12)	1.732(2)
–B(5)	1.862(2)	–B(11)	1.778(2)	–B(12)	1.850(2)	B(11)–B(12)	1.756(2)
–B(7)	1.814(2)	B(5)–B(6)	1.833(2)				

B–B Bond lengths within a B_{19} unit

B(13)–B(14)	1.759(2)	B(14)–B(17)	1.795(2)	B(17)–B(21)	1.821(2)	B(19)–B(19)	1.865(2)
–B(15)	1.818(2)	B(15)–B(18)	1.822(2)	–B(22)	1.756(2)	–B(20)	1.791(2)
–B(16)	1.822(2)	–B(19)	1.750(2)	B(18)–B(18)	1.983(3)	–B(21)	1.744(2)
–B(18)	1.844(2)	B(16)–B(17)	1.789(2)	–B(19)	1.805(2)	–B(22)	1.801(2)
–B(20)	1.904(2)	–B(10)	1.844(2)	–B(19)	1.847(2)	B(20)–B(21)	1.847(2)
B(14)–B(15)	1.874(2)	–B(21)	1.801(2)	–B(20)	1.836(2)	B(21)–B(22)	1.848(2)
–B(16)	1.735(2)						

B–B Bond lengths for linkages between units and to B(23)

B(1)–B(12)	1.715(2)	B(10)–B(10)	1.626(3)	B(6)–B(14)	1.736(2)	B(9)–B(17)	1.721(2)
B(2)–B(2)	1.809(3)	B(13)–B(21)	1.715(2)	B(7)–B(15)	1.748(2)	B(23)–B(5)	1.877(1)
B(3)–B(11)	1.688(2)	B(4)–B(16)	1.665(2)	B(8)–B(20)	1.870(2)	B(23)–B(18)	1.795(2)

Al–B and Al–Al distances[a]

Al(1)–B(14)	2.081(2)	Al(2)–B(9)	2.413(2)	Al(4)–B(8)	2.301(3)	Al(5)–B(7)	2.71 (3)
–B(5)	2.224(2)	–B(18)	2.416(2)	–B(15)	2.329(3)	–B(12)	2.80 (3)
–B(8)	2.250(2)	–B(21)	2.480(2)	–B(1)	2.377(3)	–B(19)	2.82 (3)
–B(12)	2.266(2)	–B(5)	2.510(2)	–B(12)	2.386(3)	–B(21)	2.85 (3)
–B(6)	2.300(2)	–B(13)	2.515(2)	–B(2)	2.409(3)	–B(1)	2.88 (3)
–B(20)	2.309(2)	–B(23)	2.794(1)	–B(19)	2.411(3)	–B(22)	2.93 (3)
–B(1)	2.354(2)	Al(3)–B(14)	2.044(2)	–B(20)	2.461(3)	Al(1)–Al(3)	1.230(2)
–B(18)	2.362(2)	–B(18)	2.118(2)	–B(2)	2.469(3)	–Al(4)	2.245(3)
–B(15)	2.364(2)	–B(17)	2.125(3)	–B(23)	2.623(3)	–Al(5)	0.59 (3)
–B(23)	2.366(1)	–B(13)	2.214(3)	–B(18)	2.666(3)	Al(2)–Al(2)	2.138(2)
–B(7)	2.479(2)	–B(15)	2.288(3)	–B(18)	2.819(3)	–Al(3)	2.140(3)
–B(13)	2.923(2)	–B(21)	2.319(3)	Al(5)–B(14)	1.98 (2)	–Al(4)	2.478(3)
–B(17)	2.928(2)	–B(22)	2.338(2)	–B(18)	2.15 (2)	–Al(5)	2.68 (3)
Al(2)–B(22)	2.192(2)	–B(19)	2.446(3)	–B(15)	2.26 (2)	Al(3)–Al(5)	0.64 (3)
–B(2)	2.251(2)	–B(23)	2.491(2)	–B(20)	2.32 (2)	Al(4)–Al(5)	2.71 (3)
–B(2)	2.265(2)	–B(20)	2.517(3)	–B(23)	2.33 (2)		
–B(17)	2.280(2)	–B(6)	2.908(3)	–B(17)	2.51 (3)		
–B(15)	2.309(2)	Al(4)–B(7)	2.244(3)	–B(13)	2.53 (3)		
–B(7)	2.342(2)	–B(5)	2.247(3)	–B(6)	2.54 (3)		
–B(17)	2.379(2)	–B(3)	2.267(3)	–B(5)	2.55 (3)		
–B(9)	2.384(2)	–B(11)	2.275(3)	–B(8)	2.59 (3)		

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[a] All distances less than 3.0 Å are included.

In that connection, the known structure of α-AlB$_{12}$ does not fulfill those expectations; on the contrary, it emphasizes the need for separate detailed structural analysis from single crystals for the other related substances, as we shall now demonstrate.

It is a reasonable assumption that a common feature to all the above structures is a boron framework since in α-AlB$_{12}$ all the outwardly directed bonds for the B$_{12}$ and B$_{19}$ units are shared with boron and *not* with aluminum atoms. If we take both the icosahedral and the B$_{19}$ units as comprising that framework, then for β-tetragonal boron it is not obvious where to place the additional boron atoms. The aluminum sites of α-AlB$_{12}$ are hardly appropriate and no other clear choice is indicated. In the case of "BeB$_6$" it would be more reasonable to assume a distribution of Be among the Al sites, since the distances indicated for Be–B and Be–Be would be acceptable. There are several ways of doing that, resulting in a stoichiometry close to but not exactly that given by Sands *et al.* (*6*); e.g., full occupancy of Al(1), Al(2), and Al(4) to give a total of 24 Be atoms per unit cell. Despite the uncertainties and ambiguities in this procedure, we have made calculations of the expected Debye–Scherrer patterns for comparison with the published observed values.

In the case of "BeB$_6$," we have considered many models which maintained the boron framework and made use of different Al sites, but allowed various redistributions of boron atoms among B$_{19}$ sites and the Al sites, allowing for a total of 24 to 32 beryllium atoms. In no case was there the slightest kind of agreement with the observed intensities. It seemed that any use of the Al sites, whether for Be or B, was detrimental for reproducing the observed intensities. Our conclusion is that sites other than those for Al in α-AlB$_{12}$ may be occupied and that there may even by some question as to the occurrence of the B$_{19}$ unit in "BeB$_6$." Perhaps the only common feature of these structures is the presence of the icosahedral chains. At any rate, single-crystal data are more desirable than ever for "BeB$_6$."

As to boron itself, i.e., the β-tetragonal form, it is clear that there is no hope of matching powder intensities making use only of the sites found in α-AlB$_{12}$. It would be strange, of course, if boron atoms were in the exact aluminum sites of α-AlB$_{12}$. There is not sufficient indication, however, from the AlB$_{12}$ structure as to what modifications should be made in order to accommodate extra boron atoms.

In conclusion, then, instead of indicating immediately the structures of β-tetragonal boron and the other seemingly related structures, the knowledge of the α-AlB$_{12}$ structure raises new questions regarding the nature of these structures, whose answers can be provided only by X-ray diffraction studies of single crystals. For such studies the known boron framework in α-AlB$_{12}$ should be quite helpful in achieving the complete structure solution.

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