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Single-Crystal X-ray Diffraction Study of AlB_{31} of the β-Rhombohedral Boron Structure

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The structure of a crystal with the composition AlB_{31}, prepared by arc-melting crystals of α-AlB_{12}, has been investigated by single-crystal X-ray diffractometry. The space group is $R\bar{3}m$ (No. 166) with the hexagonal cell dimensions a = 10.965(1) Å and c = 23.868(2) Å. The structure was refined by a full-matrix least-squares program to an $R(R_w)$ value of 0.034(0.040). The three-dimensional boron framework of the crystal is essentially equivalent to that of β-rhombohedral boron. The aluminum atoms partially occupy A_1 and D holes in the boron framework, and in the D hole the aluminum atoms are distributed over five positions. A disordered structure around the single B(15) atom site is discussed in connection with the Al distribution in the D hole. © 1989 Academic Press, Inc.

1. Introduction

The complete structure determination of β-rhombohedral boron was published in 1970 (*1*) and almost at the same time the structural studies of the two crystals of the β-rhombohedral boron structure, CrB_{41} (*2*) and $Cu_2Al_{2.7}B_{104}$ (*3*), were reported. After that numerous kinds of crystals of the same type have been studied by single-crystal X-ray diffractometry. The crystals studied so far were solid solutions of 3d elements and of Zr, Si, and Ge (*4*). The significant feature of these materials is that the three-dimensional boron frameworks in the crystals are retained almost unchanged from that in β-rhombohedral boron, and that the metals or p element atoms partially occupy some interstitial holes in the boron framework with various occupancies.

In the present work we studied the structure of AlB_{31} which has been obtained by

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arc-melting crystals of α-AlB$_{12}$. In an earlier paper (5), the melting point of α-AlB$_{12}$ was reported to be 2150 ± 50°C, and subsequently it was found that α-AlB$_{12}$ decomposes close to this melting point, separating elementary aluminum atoms. The present paper reports that the product material formed by the decomposition of α-AlB$_{12}$ is of the β-rhombohedral boron type structure, and presents a description of the nature of metal distribution in the boron framework.

2. Experimental

2.1. *Preparation and Phase Analysis*

Crystals of α-AlB$_{12}$ were prepared by high-temperature aluminum solution growth technique. The claimed purities of the starting materials were 99.5 and 99.99% for boron and aluminum, respectively. The crystals of α-AlB$_{12}$ were crushed in a steel mortar into a fine powder, which was then treated with hydrochloric acid to eliminate the iron impurity from the steel mortar. The powder of α-AlB$_{12}$ was washed with distilled water repeatedly and dried in air at room temperature. A pellet prepared by pressing about 1 g of the powder material was placed on the water-cooled pedestal in an arc-furnace, melting under an atmosphere of purified argon, and then cooled very rapidly by cutting off the powder supply to the furnace. The arc-melted sample was examined by X-ray powder diffraction using a Guiner-Hägg camera with pure Cu$K\alpha_1$ radiation and found to consist of a phase of the β-rhombohedral boron type structure and a small amount of elementary aluminum.

2.2. *X-Ray Measurements*

The crystal used was approximately spherical and had an average diameter of 0.3 mm. It was selected from the crystal fragments which were produced by crushing the arc-melting material. The preliminary precession photographs showed that the crystal was the same phase as the powder material which was identified by a Guiner-Hägg photograph to be of the β-rhombohedral boron type structure. The least-squares refinement of the setting angles of 23 reflections within 22°–30° in 2θ, measured with a Rigaku AFC-4 four-circle diffractometer with graphite-monochrommated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), yielded the hexagonal lattice constants $a = 10.965(1)$ Å and $c = 23.868(2)$ Å. A total of 3879 reflections with $0 \leq h \leq 17$, $-17 \leq k \leq 17$, $0 \leq l \leq 38$, for which $2\theta < 70°$, was measured by the ω scan ($2\theta \leq 30°$) and $\omega - 2\theta$ scan ($2\theta > 30$) methods, with a scan speed of 2° min^{-1} in ω. The ordinary Lorentz and polarization corrections were applied, but no corrections for the absorption effect ($\mu = 1.79$ cm^{-1}, $\mu r = 0.03$) were made. Reflections with $F_o < 3\sigma(F_o)$ were excluded from the data and a total of 1181 unique reflections was obtained by averaging the F_o values for equivalent reflections.

3. Structure Analysis

The structure was solved by the iterative difference Fourier method starting with atomic parameters of boron (B(1)–B(15)) in NiB$_{48.5}$ (7) whose boron framework is essentially the same as that in β-rhombohedral boron. A difference Fourier synthesis, calculated on the basis of the boron framework, showed two strong electron density maxima. The first maximum centered at the A_1 hole (6c position; 0, 0, 0.134) on the $\bar{3}$ axis. The second was at the D hole (18h position; 0.200, $-x$, 0.180) on a mirror plane and was very broad, suggesting that the Al site in the D hole is split into two or more positions. (For the notation of the holes see Ref. (2).) Assuming two Al atoms, Al(1) at the A_1 hole and Al(2–1) at the center of D hole, the structure was refined with isotropic temperature factors including occupancies of B(13), Al(1), and Al(2–1), by the full-matrix least-squares program. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were $1/\sigma^2(F_o)$. The R values, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, obtained were 0.083 and 0.077, respectively. A difference synthesis calculated subsequently gave four extra residual peaks around the Al(2–1) site of which two were independent due to their location off the mirror plane. A further least-squares refinement including the two new sites, Al(2–2) and Al(2–3), strongly lowered the $R(R_w)$ value to 0.038(0.041). In subsequent difference synthesis, no significant residual peaks were found but that (1.0 e Å^{-3}) around the B(15) site. Therefore, a final refinement of the structure was performed applying anisotropic temperature factors to the B(15) atom; the $R(R_w)$ value decreased to 0.034(0.040).

The isotropic extinction parameter g was introduced at the final stage of refinement, but no improvement of the $R(R_w)$ value was obtained; as the parameter g adopted a negative value within one standard deviation, it was fixed at zero. Application of anisotropic temperature factors to the Al(1) atom did not result in a lowering of the $R(R_w)$ value, reflecting the nearly isotropically truncated tetrahedral form of the A_1 hole. Anisotropic temperature factors were not applied to the Al(2–1, 2, 3) atoms because of their low occupancies. In order to see a possibility of the incorporation of a boron atom into the Al(2–3) site, which possesses an unusually short distance from the B(15) atom, a least-squares refinement was performed by replacing the aluminum atom with a boron atom. However, for the Al(2–2) atom situated in the vicinity of the boron atom placed at the Al(2–3) site the refinement gave a negative value of temperature factor. Therefore, the Al(2–3) site was not assumed as being occupied by a boron atom but by an aluminum atom. We have also performed a least-squares refinement by putting boron atoms at both the (2–2) and Al(2–3) sites. In this case, the refinement gave negative values of temperature factors for the two boron atoms. By putting Al atoms at both sites, we could obtain reasonable positive temperature factors for the two aluminum atoms. These least-squares refinements support our assignment of Al(2–3) site. A detailed discussion about this site will be given in the next section.

The atomic scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-Ray Crystallography" (1974) (*8*). All the calculations for the structure analysis were made by using the Program UNICS-III (*9*).

4. Results and Discussion

Detailed descriptions of the structure of β-rhombohedral boron were given by Hoard *et al.* (*1*) and an accurate refinement of the structure was later performed by Callmer (*10*). The β-rhombohedral boron structure is made up of two crystallographically different kinds of B_{12} icosahedra, a B_{28} unit, and a single B atom. The numbering scheme for the boron atoms in Table I is the same as that used by Hoard *et al.* and by Callmer. The B_{12} icosahedra consist of B(1, 2, 5, 6, 7, 9) atoms and the B_{28} unit of B(3, 4, 8, 10, 11, 12, 13, 14) atoms. The single B atom is designated B(15).

(*1*) *Boron atoms.* A comparison of the atomic coordinates of the boron atoms in AlB_{31} (Table I) with those in β-rhombohedral boron (*10*) shows that the structure of the basic boron framework is essentially the same in the two substances. The occupancy of the partially vacant framework site B(13) in the present crystal is 68.2(7)%, approximately equal to that (73.4(15)%) observed for β-rhombohedral boron. The occupancies of the same site in 3*d* element solid solutions of the β-rhombohedral boron structure are from 61 to 72% (*2, 4, 7, 11–*

TABLE I

STRUCTURE DATA FOR AlB_{31}

Atom	Site	x	y	z	Occupancy (%)	B (Å)
B(1)	36i	0.1772(2)	0.1768(2)	0.17742(6)	100	0.51(2)
B(2)	36i	0.3192(2)	0.2954(2)	0.12866(6)	100	0.47(2)
B(3)	36i	0.2612(2)	0.2172(2)	0.41971(6)	100	0.51(2)
B(4)	36i	0.2360(2)	0.2517(2)	0.34703(6)	100	0.52(2)
B(5)	18h	0.0552(1)	$-x$	−0.05534(8)	100	0.45(2)
B(6)	18h	0.0864(1)	$-x$	0.01344(8)	100	0.41(3)
B(7)	18h	0.1112(1)	$-x$	−0.11232(8)	100	0.46(3)
B(8)	18h	0.1696(1)	$-x$	0.02819(9)	100	0.49(3)
B(9)	18h	0.1290(1)	$-x$	−0.23396(8)	100	0.46(3)
B(10)	18h	0.1021(1)	$-x$	−0.30204(8)	100	0.47(3)
B(11)	18h	0.0564(1)	$-x$	0.32712(8)	100	0.45(3)
B(12)	18h	0.0899(2)	$-x$	0.39875(8)	100	0.48(3)
B(13)	18h	0.0571	$-x$	−0.44499(13)	68.2(7)	0.83(6)
B(14)	6c	0	0	0.38611(15)	100	0.45(5)
B(15)	3b	0	0	½	100	1.8(1)[a]
Al(1)	6c	0	0	0.13445(5)	85.7(4)	0.32(2)
Al(2–1)	18h	0.2005(5)	$-x$	0.1804(3)	10.5(5)	0.52(16)
Al(2–2)	36i	0.253(2)	0.449(2)	0.1679(5)	3.9(3)	0.36(30)
Al(2–3)	39i	0.306(2)	0.484(1)	0.1666(6)	3.9(3)	0.44(24)

[a] Equivalent isotropic temperature factor calculated from anisotropic temperature factor.

14), and those found in the solid solutions of Si (*15*) and Ge (*16*) are 73.9(6) and 71.6%, respectively.

The final difference synthesis was thoroughly examined to check the possibility of the presence of further interstitial atoms. Almost all of the appreciable residual peaks (0.3–0.5 e Å^{-3}) in the difference map were, however, found only about the centers of bonds between boron polyhedra, reflecting the two-centered bond nature of these intercluster B–B bonds as in α-AlB_{12} (*17*) and $LiAlB_{14}$ (*18*). The random noise peaks in the difference map were below 0.3 e Å^{-3}, which corresponds to 1.5% of a boron peak of the Fo-synthesis. No residual peak was observed at the interstitial site B(16). Recently, Slack *et al.* (*19, 20*) discovered in crystals of the β-rhombohedral boron structure five new interstitial boron sites, B(17), B(17d), B(18), B(19), and B(20), with occupancies 8.5(9), 3.2(8), 6.6(6), 6.8(6), and 3.7(4)%, respectively. As to the present crystal, however, any electron density accumulation could not be observed at these new interstitial sites.

(*2*) *Distribution of Al atoms.* The three-dimensional boron framework of β-rhombohedral boron contains at least eight interstices or holes of sufficient size to accommodate atoms (*2*). Some results on partially occupied positions from previous investigations on the solid solutions of the β-rhombohedral boron structure are summarized in Ref. (*4*) (Table 1) and Ref. (*7*) (Table 4). However, the interstices actually occupied to a certain extent by transition metal atoms or *p* element atoms are A_1, D, and E holes. In the present crystal, the Al atoms occupy only the A_1 (Al(1) site) and D (Al(2–1, 2, 3) sites) holes. Among the solid solutions whose structures were so far reported, CrB_{41} (*2*), FeB_{49} (*14*), and $NiB_{48.5}$ (*7*) showed a similar metal distribution as in the present crystal; the metal atoms in these materials are accommodated only in the A_1 and D holes. The A_1 hole is highly symmetrical, lying on the $\bar{3}$ axis with its 12 boron neighbors at the apical sites of a truncated tetrahedron. This hole is rather small in comparison with D and E holes (*2*), and this may be responsible for the fact that Sc (*11*) and Zr (*20*) atoms, having larger atomic sizes, cannot be accommodated in the A_1 hole.

A significant feature of metal distribution in AlB_{31} is that the occupancy of A_1 hole is extremely high (85.7(4)%). For CrB_{41}, FeB_{49}, and $NiB_{48.5}$, the occupancies of the A_1 hole are 71.9, 50.7, and 44.67%, respectively. Considering the larger atomic radius sum of Al and B, R(Al, 12-coordinations) + R(B) = 1.43 + 0.90 = 2.33 Å, the high occupancy of Al atoms in this small hole (2.160–2.195 Å (Table I)) is striking. The atomic radius sums of Cr–B, Fe–B, and Ni–B are 2.20, 2.16, and 2.15 Å, respectively. A similar situation is, however, found in other Al-containing B_{12}-icosahedral crystals. In the compound $LiAlB_{14}$ (*21*), for example, the Al atom is accommodated with 95.6% occupancy in a relatively small hole, being enclosed with 4B (Al–B: 2.081 Å), 2B (Al–B: 2.339 Å), and 2B (2.343 Å) atoms. As the result of a study of the valence electron distribution in $LiAlB_{14}$ by X-ray diffraction, the Al atom was found to donate a significant amount of its valence electrons (1.2 or 1.7 e) to the electron deficient boron framework (*18*). Therefore, the appreciably shorter Al–B distances in the present crystal seem to be characteristic for Al–B bond lengths in B_{12}-icosahedral materials, because the donation of valence electrons to the boron framework gives rise to a decrease of the effective atomic size of the Al atom.

Another interesting feature of the metal distribution is the splitting of the Al site in the D holes where the Al atoms are distributed over five sites, of which three are crystallographically independent; one site (Al(2–1)) is situated on the mirror plane which bisects the D hole and the other two (Al(2–2, 3)) have their respective equivalents (Al(2–2′, 3′)) through the reflection by the mirror plane. Among the other solid solutions so far reported, those containing Ni, Cu, and Ge have split sites in the D hole. In these substances, however, the number of the metal sites in the D hole is three of which two are independent. Therefore, in order to see whether the adjacent sites, Al(2–2) and Al(2–3), can be approximated by one site or not, a least-squares refinement was performed putting an Al site at the midpoint between the adjacent sites. The $R(R_w)$ value obtained was 0.048(0.044), which is significantly greater than the previous one, 0.034(0.040). A difference synthesis subsequently calculated showed prominent residual peaks (~1.2 e $Å^{-3}$) in the D hole. Therefore, the above-mentioned previous site assignments in the D hole, which imply the distributions of Al atoms over five sites (Al(2–1, 2, 2′, 3, 3′)), are considered to be plausible.

Figure 1 shows the Al distribution in the D hole, viewed down the hexagonal c axis. There are six D holes surrounding the B(15) single atom which lies at the inversion center on the threefold axis. Thus, a total of 30 aluminum sites (6 Al(2–1, 2, 2′, 3, 3′)) enclose the central B(15) atom, distributed within a height difference of $\Delta z = \pm 0.33$ Å from the z-level of the B(15) atom. If we sum the occupanies of the five Al sites, the total occupancy of each D hole by Al is 26%. The distances of Al(2–1), Al(2–2), and Al(2–3) sites from the central B(15) atom are 2.545(7), 2.09(3), and 1.87(2) Å, respectively (Table II). Since the Al–B distances so far found in Al-containing B_{12}-icosahedral crystals were greater than 2.0 Å, the value of 1.87(2) Å for the Al(2–3)–B(15) distance is too short for an Al–B bond length. However, it seems to be possible to interpret this unusual value of an Al–B distance in terms of a static disorder model for the B(15) site presented below.

TABLE II

Interatomic Distances in AlB_{31}

B–B distances (<1.95 Å)

B(1)–B(2)	1.820(2)	B(5)–B(7)	1.726(3)	B(10)–B(8)	1.841(3)
–B(9)	1.829(3)	–B(6)	1.745(3)	–2B(4)	1.842(3)
–B(2)	1.856(2)	–2B(6)	1.752(3)	B(11)–B(14)	1.770(4)
–B(7)	1.879(3)	–2B(5)	1.815(3)	–2B(10)	1.785(3)
–B(1)	1.934(2)	B(6)–B(8)	1.619(3)	–B(12)	1.824(3)
–B(1)	1.948(2)	–B(5)	1.745(3)	–2B(4)	1.850(3)
B(2)–B(3)	1.725(2)	–2B(5)	1.752(3)	–2B(11)	1.856(3)
–B(7)	1.793(3)	–2B(6)	1.762(3)	B(12)–B(14)	1.734(4)
–B(1)	1.820(2)	B(7)–B(5)	1.726(3)	–2B(3)	1.782(3)
–B(2)	1.834(2)	–2B(2)	1.793(3)	–B(11)	1.824(3)
–B(9)	1.852(3)	–B(9)	1.797(3)	–2B(4)	1.857(3)
–B(1)	1.856(2)	–2B(1)	1.879(3)	–2B(13)	1.859(4)
B(3)–B(2)	1.725(3)	B(8)–B(6)	1.619(3)	B(13)–B(15)	1.703(3)
–B(12)	1.782(3)	–2B(4)	1.739(3)	–B(14)	1.775(5)
–B(13)	1.793(4)	–2B(3)	1.797(3)	–2B(3)	1.793(4)
–B(8)	1.797(3)	–B(10)	1.841(3)	–2B(12)	1.859(3)
–B(4)	1.826(2)	B(9)–B(10)	1.703(3)	–2B(13)	1.879(5)
–B(3)	1.900(3)	–B(7)	1.797(3)	B(14)–3B(12)	1.734(4)
B(4)–B(4)	1.683(2)	–2B(1)	1.829(3)	–3B(11)	1.770(4)
–B(8)	1.739(3)	–2B(2)	1.852(3)	–3B(13)	1.775(5)
–B(3)	1.826(2)	B(10)–B(9)	1.703(3)	B(15)–6B(13)	1.703(3)
–B(10)	1.842(3)	–2B(11)	1.785(3)		
–B(11)	1.850(3)				
–B(12)	1.857(3)				

Al–B distances (<2.54 Å)

A(1)–3B(5)	2.160(2)	Al(2–1)–B(15)	2.545(7)	Al(2–3)–B(13)	1.63(2)
–3B(7)	2.176(2)	Al(2–2)–B(13)	1.69(3)	–B(13)	1.79(2)
–6B(1)	2.195(2)	–B(3)	2.09(3)	–B(15)	1.87(2)
Al(2–1)–B(13)	2.182(8)	–B(13)	2.09(3)	–B(3)	2.07(2)
–B(12)	2.243(8)	–B(15)	2.09(3)	–B(3)	2.17(2)
–2B(1)	2.342(8)	–B(3)	2.32(3)	–B(2)	2.32(2)
–2B(3)	2.353(8)	–B(2)	2.33(3)	–B(2)	2.35(2)
–2B(2)	2.357(8)	–B(3)	2.36(3)	–B(13)	2.42(2)
–2B(13)	2.404(8)	–B(13)	2.36(3)	–B(12)	2.52(2)
–2B(3)	2.437(8)	–B(2)	2.40(3)		
–2B(2)	2.462(8)	–B(12)	2.44(3)		

Al–Al distances (<2.65 Å)

Al(2–1)–2A(l(2–2)	0.63(3)	Al(2–2)–Al(2–3)	1.07(3)	Al(2–3)–Al(2–3)	0.51(3)
–2Al(2–3)	1.11(3)	–Al(2–2)	1.52(4)	–Al(2–2)	1.02(3)
–2Al(2–3)	1.59(3)	–Al(2–3)	1.58(3)	–Al(2–2)	1.07(3)
–2Al(2–2)	2.07(2)	–Al(2–1)	2.07(3)	–Al(2–1)	1.11(2)
–2Al(2–1)	2.61(1)	–2Al(2–2)	2.09(4)	–Al(2–3)	1.41(3)
–2Al(2–2)	2.65(3)	–Al(2–3)	2.34(3)	–Al(2–2)	1.58(3)
Al(2–2)–Al(2–3)	0.51(3)	–Al(2–3)	2.38(3)	–Al(2–1)	1.59(2)
–Al(2–1)	0.63(3)	–Al(2–2)	2.61(4)	–2Al(2–3)	1.87(3)
–Al(2–2)	0.63(4)	–Al(2–1)	2.65(3)	–Al(2–3)	2.30(3)
–Al(2–3)	1.02(3)	Al(2–3)–Al(2–2)	0.51(3)	–Al(2–2)	2.38(3)

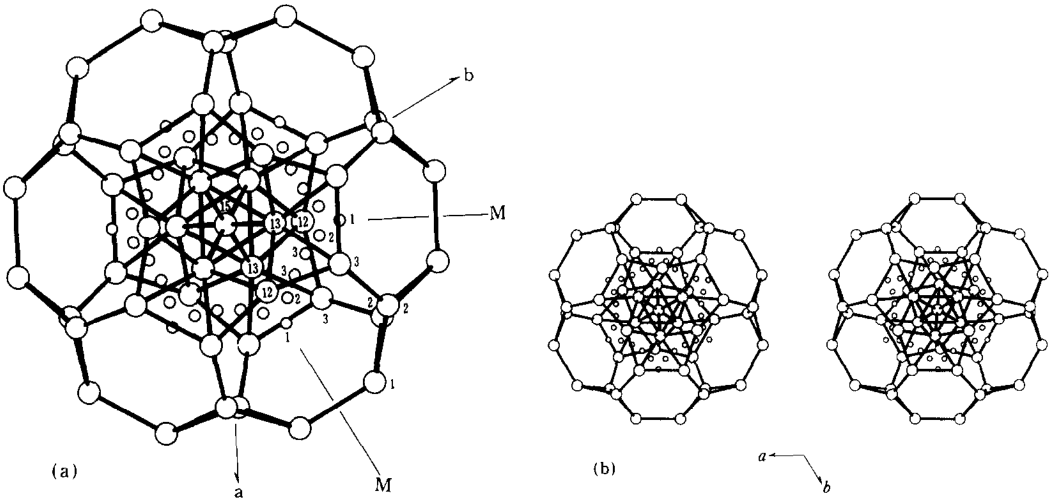

FIG. 1. (a) A partial structure around the B(15) atom as seen along the hexagonal *c* axis. The larger circles represent boron atoms, and the small circles designated 1, 2, and 3 indicate Al(2–1), Al(2–2), and Al(2–3) atoms, respectively. The B(15) atom lies at the inversion center on the threefold axis. (b) Stereoscopic view of the partial structure.

The temperature factor of the B(15) atom is very large (Table I), and in addition a marked anisotropy is shown in the data of the root mean square displacements obtained for this atom: $\sqrt{U_{11}} = 0.184(10)$ Å, $\sqrt{U_{22}} = \sqrt{U_{11}}$, $\sqrt{U_{33}} = 0.037(0.032)$ Å, $\sqrt{U_{12}} = \frac{1}{2}(\sqrt{U_{11}})$, $\sqrt{U_{13}} = 0$, $\sqrt{U_{23}} = 0$. Figure 2 shows a thermal motion of B(15) calculated from the above data and the nature of coordinations of Al(2–3) sites around the B(15) atom. All the Al atoms are almost on the same *z*-level as the B(15) atom. The occupancy of the Al(2–3) site as well as that of its adjacent site (Al(2–2) is only 3.9% (Table I); i.e., most of the Al(2–3) and Al(2–2) sites are vacant. When an Al(2–3) atom is brought into the structure, the nearest neighbor B(15) atom is probably shifted in such a direction that Al–B distances shorter than 2.0 Å are avoided. In consequence, over the whole crystal random shifts of the B(15) site necessarily occur approximately in parallel with the hexagonal (001) plane, giving rise to seemingly strong and anisotropic thermal vibrations. The disorder model presented seems to represent the partial structure surrounding the central B(15) atom, since both the unusual Al–B bond length and the thermal parameters of the B(15) atom are reasonably well interpreted. Furthermore, the B(13) site enclosing octahedrally the B(15) site is not fully occupied (occupancy: 68.2(7)%), which should make the B(15) site easier to be shifted from its normal position. However, one must keep in mind that the X-ray diffraction experiment gives solely the electron density distribution. For a partially occupied position crystal-chemical arguments must then be used to clarify which element is most probably accommodated at a certain position. It was suggested by a referee that the Al(2–3) position might accommodate boron instead of aluminum atoms. One can even imagine a mixed occupancy by boron and aluminum. These possibilities were, however, regarded by us as less plausible for the reasons above.

The chemical composition of the present crystal calculated from the result of the structure analysis (Table I) is $AlB_{31.4\pm1.0}$, in good agreement with $AlB_{29.2\pm1.4}$ observed

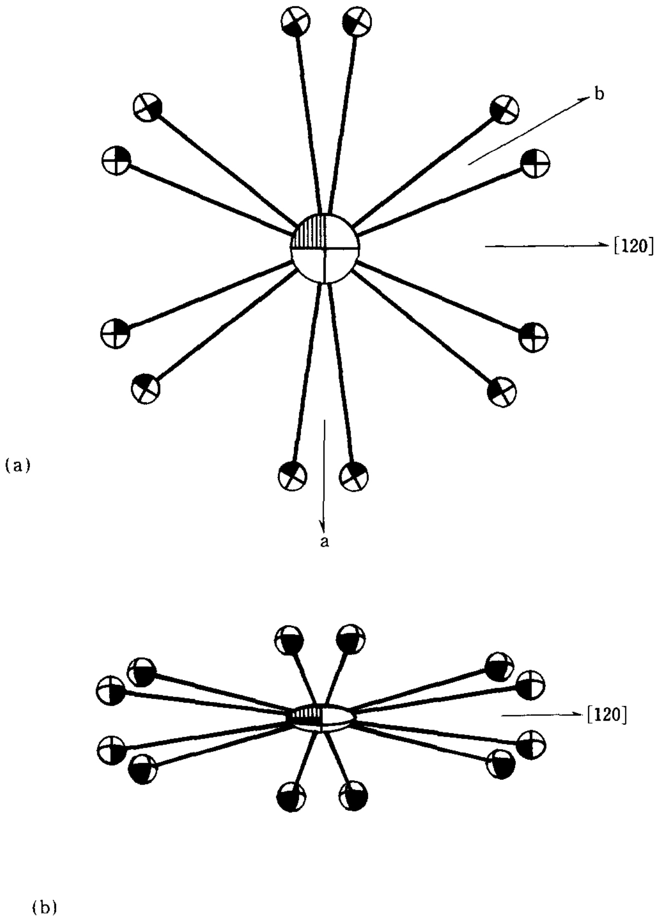

FIG. 2. The coordinations of Al(2–3) atoms around the B(15) atom. The figure in (a) is projected on a plane parallel to the (001) plane along the hexagonal *c* axis, and that in (b) is projected on the same plane after rotating the figure in (a) by +70° about the [120] axis. Thermal ellipsoids are drawn at the 50% probability level.

subsequently for a second crystal from the same batch, from which the first one had been selected. The conditions of intensity data collection were the same for both crystals. The $R(R_w)$ value obtained for the second crystal was 0.051(0.044). The structure of the second crystal studied is the same as that of the first one in every respect. This is somewhat unexpected, since a solidified arc-melted sample is normally not in thermal equilibrium due to different cooling rates (the top of the sample cools more slowly than the bottom). Therefore the distribution of the aluminum atoms obtained does not necessarily represent equilibrium.

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