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Presence of Carbon in Aluminum Borides

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The effect of carbon on the formation of the reported phases in the aluminum–boron system was investigated. The results indicate that there are only three pure binary aluminum borides, AlB_2, α-AlB_{12}, and γ-AlB_{12}. The phase referred to in the literature as β-AlB_{12} was found to correspond to a stoichiometry $C_2Al_3B_{48}$; however, X-ray analysis of this material indicated the presence of two phases. The two phases are derived from a single high temperature phase with a composition of $C_2Al_3B_{48}$ which disproportionates on cooling. The phase referred to in the literature as AlB_{10} was found to correspond to a stoichiometry C_4AlB_{24}. This composition was confirmed by a structure analysis. Both ternary, Al–B–C, phases have an integral number of formula units per crystallographic unit cell. A new ternary phase corresponding to the formula $Al_4C_4B_{1-3}$ has been discovered. A method for preparation of crystals of each phase is described.

Introduction

A general program on preparation of high purity refractory borides is currently in progress at this laboratory. This paper describes the work on synthesis and identification of the various phases of aluminum boride and the possible role of carbon in their formation.

During the past hundred years a number of binary compounds of aluminum and boron have been reported in the literature.[1–8] Six compounds with different crystallographic phases have been described and the existence of these six phases appears to be well corroborated. On the other hand, a wide variance of opinion exists as to the chemical composition of these compounds. The most recent interpretation by Kohn, *et al.*,[6–8] indicates that of the six reported phases, AlB_2, AlB_{10}, α-AlB_{12}, β-AlB_{12}, γ-AlB_{12}, and monoclinic AlB_{12}, the first five represent true binary compounds while the monoclinic AlB_{12} is actually a modification of elemental boron.

The variance of opinion as to stoichiometry very likely derives from the fact that, in a typical synthesis, several phases are frequently obtained at the same time and separation of crystals must be carefully done under a microscope. As a result, chemical analysis is made on a few milligrams of crystals which are usually handpicked. An additional complication arises from the presence of carbon impurities; thus in the case of β-AlB_{12}, Náray-Szabó[9] described this material as a mixture of AlB_{12} and B_4C in the ratio of 3/2. Kohn, *et al.*,[6] on the other hand, did not observe any carbon while Biltz[3] assigned the formula $C_2Al_3B_{44}$ or $C_2Al_3B_{48}$ to these crystals.

Because of this confusion, it was decided to synthesize these compounds in sufficient quantity in order to establish their composition.

Results

In this work five phases have been isolated and identified on the basis of crystallographic descriptions available in the literature. With respect to composition, however, there appear to be only three binary aluminum–boron compounds. The evidence indicates that two of the other reported compounds are ternary phases derived from Al–B–C systems. Monoclinic AlB_{12} was not observed, which is in agreement with Kohn, *et al.*[6] A new ternary phase of Al–B–C has been discovered and is reported here.

The crystallographic assignments for these five phases plus the newly reported one are summarized in Table I.

TABLE I

BINARY ALUMINUM–BORON AND TERNARY ALUMINUM–BORON–CARBON COMPOUNDS

	Composition		Crystallographic data[a]		
	Previous work	This work	System	Space group	Dimensions, Å.
1	AlB_2	$Al_{0.9}B_2$	Hexagonal[11]	C6/mmm	$a = 3.009$ $c = 3.262$
2	α-AlB_{12}	α-AlB_{12}	Tetragonal[7]	$P4_12_12$ or $P4_32_22$	$a = 10.161$ $c = 14.283$
3	γ-AlB_{12}	γ-AlB_{12}	Orthorhombic[8]	$P2_12_12_1$	$a = 16.56$ $b = 17.53$ $c = 10.16$
4	$C_2Al_3B_{44}$ $C_2Al_3B_{48}$ (β-AlB_{12})	$C_2Al_3B_{48}$	Orthorhombic[7]	12/m2/m2/a[b]	$a = 12.34$ $b = 12.631$ $c = 10.161$
5	(AlB_{10})	C_4AlB_{24}	Orthorhombic[6,10]	$B2/b2_1/m2/m$ or $Bb2_1m$	$a = 8.881$ $b = 9.100$ $c = 5.690$
6	...	$C_4Al_4B_{1-3}$	Hexagonal	P6/mcm or $P\bar{6}c2$ or $P\bar{3}c1$	$a = 5.90$ $c = 15.90$

[a] With the exception of item 6, all crystallographic data have been obtained from literature as indicated. [b] After this article was submitted a detailed examination of the unit cell of this material uncovered discrepancies with the literature and a short review of the results is given in the last section of this article.

The preferred formulas for these phases based on this study are indicated in column 2 while those in column 1 represent compositions which have been reported to date.

Discussion

A. $Al_{0.9}B_2$(AlB_2).—The data in the literature[11] relating to the crystallography of AlB_2 were confirmed. The chemical analysis, on the other hand, was found to correspond more closely to $Al_{0.90}B_2$ than to AlB_2. The theoretical composition of AlB_2 as well as the theoretical density of 3.17 g./cc. have never been experimentally established. The density of 2.955 g./cc. found here is in excellent agreement with the formula $Al_{0.9}B_2$. The only other reported experimental value of density is in fact lower (2.84 g./cc.),[12] apparently due to the presence of aluminum impurities. Thus

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(1) H. Saint-Claire Deville and F. Woehler, *Ann. Physik*, **100**, 635 (1857).

(2) W. Hampe, *Justus Liebigs Ann. Chem.*, **183**, 75 (1876).

(3) H. Biltz, *Ber.*, **41**, 2634 (1908); **43**, 297 (1910).

(4) F. Woehler, *Justus Liebigs Ann. Chem.*, **141**, 268 (1867).

(5) F. Halla and R. Weil, *Naturwissenschaften*, **27**, 96 (1939), *Z. Kristallogr.*, **101**, 435 (1939).

(6) J. A. Kohn, G. Katz, and A. A. Giardini, *ibid.*, **111**, 53 (1958).

(7) J. A. Kohn and D. W. Eckart, *Anal. Chem.*, **32**, 296 (1960).

(8) J. A. Kohn and D. W. Eckart, *Z. Kristallogr.*, **116**, 134 (1961).

(9) St. v. Náray-Szabó, *ibid.*, **94**, 367 (1936).

(10) G. Will, *J. Am. Chem. Soc.*, **85**, 2335 (1963).

(11) E. J. Felton, *ibid.*, **78**, 5977 (1956).

(12) W. Hofmann and W. Jäniche, *Z. physik. Chem.*, **31**, 214 (1936).

while one may be inclined to interpret the present finding as an aluminum-low sample of AlB_2, there is no evidence that a sample with a higher aluminum content can be prepared.

B. α-AlB_{12}.—This compound was obtained in the form of tetragonal crystals. Both the crystallographic and chemical analyses corroborated those already reported in the literature.[5,7]

C. γ-AlB_{12}.—This phase which was recently discovered by Kohn and Eckart[8] possesses an orthorhombic structure. It is related to the α-AlB_{12} in that the γ-phase can be geometrically derived from the α-phase.[8] The two phases tend to form intertwinned crystals and as a result the γ-AlB_{12} has apparently never been prepared without the presence of at least small quantities of the α-phase.

D. $C_2Al_3B_{48}$ (β-AlB_{12}).—This phase, which was originally described as a diamond-like boron, is obtained in the form of amber crystals. A variety of compositions have been ascribed to this material. Biltz[3] proposed a formula of $C_2Al_3B_{44}$ or $C_2Al_3B_{48}$ for this phase. In a later investigation Náray-Szabó[9] concluded that this compound was a binary aluminum boride with a composition of AlB_{12}. The presence of carbon in Biltz's product was explained on the basis that $C_2Al_3B_{44}$ could be rewritten as $3AlB_{12} \cdot 2B_4C$. Náray-Szabó proposed that such a phase might result from regularly intergrown layers of AlB_{12} and B_4C. Recently Kohn, Katz, and Giardini[6] have supported the contention that this phase is a binary aluminum boride and have referred to it as β-AlB_{12}. In all these cases the crystallographic assignments and descriptions agreed at least to the extent that there could be no question as to the identity of the compounds prepared in the three investigations. Our efforts to prepare this material have resulted in a compound with a composition which is very close to $C_2Al_3B_{48}$. This is in agreement with one of the two formulas proposed by Biltz. It was found that this phase could not be obtained by reaction of aluminum and boron only. On the other hand, it was readily obtained by addition of a controlled amount of carbon to the reactants. Thus, in a typical experiment, with traces of carbon present, this phase was found to contain about 3% carbon while other phases from the same batch contained less than 0.2% carbon.

The apparent contradictions that exist in the composition reported earlier may be rationalized in the following manner. Náray-Szabó contended that the material was a mixture of AlB_{12} and B_4C on the basis that treatment with fuming nitric acid under pressure led to a product which under chemical analysis showed increased aluminum and decreased carbon content. Assuming the remainder to be boron, Náray-Szabó obtained a ratio of B/Al of 11/1 to 12/1. Several objections can be made to this conclusion: (1) The presence of approximately 20% B_4C in a mixture of phases should be easily detected by X-ray examination. This has never been observed. (2) The material after treatment with fuming nitric acid was not characterized crystallographically. Indeed, since boron was determined by difference, formation of some Al_2O_3 during the treatment would have yielded the same results. Finally, Náray-Szabó points out that Biltz's proposed composition of $C_2Al_3B_{44}$ does not correspond to an integral number of molecules per unit cell. Although this does not have to be satisfied, it can readily be seen that use of Biltz's alternate composition $C_2Al_3B_{48}$ results in almost exactly four molecules per unit cell.

In the more recent work of Kohn, Katz, and Giardini[6] this phase was described as a binary aluminum boride with a composition of AlB_{12}. This composition could not be confirmed on the basis of the present work. In view of the close agreement between the present findings and the compositions assigned by Biltz,[3] and the fact that Kohn, *et al.*,[6] based their stoichiometric assignment on analysis of a very small sample (about 30 mg.), the authors feel that the discrepancy may be attributed to the difficulties connected with analysis of samples of that size.

E. C_4AlB_{24}(AlB_{10}).—This phase was reported for the first time in 1958 by Kohn, Katz, and Giardini.[6] They assigned a formula of AlB_{10} to this compound and presented details as to morphology, appearance, and unit cell dimensions. More recently Will[10] has reported a preliminary structure determination of this phase.

Samples crystallographically identical with those described as AlB_{10} have been successfully prepared in our study. However, the stoichiometry could not be confirmed. As in the above-described case, this phase could not be prepared by reaction of aluminum and boron alone. In fact, considerably greater quantities of carbon were required than that needed for preparations of $C_2Al_3B_{48}$. A composition of C_4AlB_{24} was indicated for this phase. Densities from 2.48 to 2.57 g./cc. have been observed. On the basis of these values, the unit cell contains two molecules of C_4AlB_{24}. Thus, contrary to some earlier reports,[6,8] neither $C_2Al_3B_{48}$ nor C_4AlB_{24} phases have an anomalous number of formula units per crystallographic unit cell. A detailed structure analysis has been undertaken in this laboratory and the icosahedral grouping of boron atoms reported by Will[10] is confirmed. A short structure description is given in the last section of this article.

F. $Al_4C_4B_{1-3}$.—This material is a new phase which occurs in the form of yellow, plate-like crystals and appears to possess a variable boron content. The variation in boron indicates existence of a homogeneity range; however, the limits of composition have not as yet been established. Within observed variations the system seems to extend from a composition of Al_4C_4B to one of $Al_4C_4B_3$.

Morphologically the crystals appear as hexagonal plates with only pinacoidal (001) and prismatic (100) faces. Under X-ray examination some crystals display either doubled or diffused points on the film. This distortion may be connected with the observed variations in stoichiometry and may indicate some structural differences between the two components involved in this homogeneity range. The crystals without distortions were found to be hexagonal with $a = 5.90$ Å. and $c = 15.90$ Å. On the basis of systematic extinctions, the possible space groups are: $P6/mcm$, $P\bar{6}c2$, or $P\bar{3}c1$. The density was found to vary between 2.48 and 2.67 g./cc. which is in agreement with the variable composition of the samples. The unit cell contains four molecules. Some of the X-ray powder diffraction lines are listed in Table II.

TABLE II

X-RAY POWDER DIFFRACTION LINES OF $Al_4C_4B_{1-3}$ OBTAINED BY USE OF FILTERED Cu RADIATION AND STRIP CHART RECORDER

h,k,l	I/I_1[a]	d, measd., Å.	d, calcd., Å.
0,0,2	90	7.95	7.95
0,0,4	70	3.97	3.97
1,1,0	10	2.95	2.95
1,1,1	30	2.90	2.90
0,0,6	100	2.64	2.65
1,1,3	5	2.58	2.58
1,1,4	15	2.37	2.37
1,0,6			2.35
1,1,5	1	2.16	2.16
0,0,8	90	1.98	1.99
1,1,6			1.97
1,1,7	40	1.80	1.80
3,0,0	40	1.70	1.70
1,1,9	15	1.52	1.52
1,2,7	2	1.47	1.47
2,2,1			1.47
3,0,6	1	1.434	1.433
2,2,3	1	1.418	1.421
2,2,4	5	1.385	1.383
1,1,11	10	1.296	1.298
3,0,8	2	1.292	1.293
2,2,6			1.289
1,1,12	20	1.208	1.209

[a] Relative intensity of lines.

It should be clearly pointed out that in the present work the investigation was limited to an examination of the role of carbon in aluminum borides. In this type of compound the interstitial carbon[13] can often be replaced by other elements such as oxygen and nitrogen. As a consequence, other series of ternary aluminum–boron compounds may exist and, in fact, may have been present in some compounds reported earlier as binary phases.

Experimental

General Procedure.—In all of the preparations the starting materials consisted of high purity aluminum, boron, and carbon. They were mixed in the proportions as described. Zirconia crucibles were used in experiments requiring temperatures of up to 1400°, and at higher temperatures boron nitride crucibles were used. In specific cases where the presence of carbon was desired, graphite crucibles could be used in place of the additional carbon. Prior to firing, the samples were evacuated in a bell jar and placed under an argon atmosphere. Induction heating with graphite susceptors was used in the bell jar to fire the samples. The excess aluminum which was present as a solvent was dissolved in hydrochloric acid. The +20 mesh crystals were separated by screening and generally used throughout this study. Subsequent physical separation of the various phases was thus simplified by use of the relatively large crystals. The yields which are based on the original boron content relate only to the +20 mesh fraction of a given phase, after separation. Microscopic and X-ray examinations were used to confirm the presence of a single phase in each case.

AlB_2.—The AlB_2 phase was prepared by fusing a mixture of aluminum (320 g.) and boron (4.0 g.) in a zirconia crucible at 1200° for 8–12 hr. The melt was cooled at a rate of about 100° per hour in order to obtain larger crystals. The sample was treated with dilute hydrochloric acid and in a few minutes thin flakes of AlB_2 up to 2 mm. in diameter could be observed floating in the beaker. The crystals are slowly attacked by acid and must be continually removed from the beaker and washed with water. Small amounts of other aluminum borides are readily removed by screening and separation in heavy liquids. The yield of AlB_2 was 5%. The absence of other phases was confirmed by microscopic and X-ray examination. The density of the crystals was found to be 2.955 g./c.

Anal. Calcd. for AlB_2: Al, 55.51; B, 44.49. Found: Al, 52.98; B, 47.00. Calcd. for $Al_{0.9}B_2$: Al, 52.90; B, 47.10.

α-AlB_{12}.—This compound was prepared by fusion of a mixture of 300 g. of aluminum and 75 g. of boron in a boron nitride crucible at 1700° for 1–3 hr. The sample was allowed to cool to room temperature in 3–4 hr. A slower rate of cooling should be avoided as it results in formation of the γ-AlB_{12} phase. Excess aluminum was dissolved in hydrochloric acid and the −20 mesh fraction was removed by screening. The +20 mesh fraction which consists of pure α-AlB_{12} was obtained in a 40% yield. A few amber crystals of another phase that are occasionally observed can be easily removed under a magnifying glass. The analysis of the sample confirms the AlB_{12} stoichiometry. Up to 0.2% carbon could frequently be detected as major impurity. This impurity probably derived from the use of graphite susceptors.

Anal. Calcd. for AlB_{12}: Al, 17.19; B, 82.81. Found: Al, 16.90; B, 82.52.

γ-AlB_{12}.—A sample of γ-AlB_{12} containing small amounts of the α-phase was prepared by fusing together a mixture of 400 g. of aluminum and 20 g. of boron at 1400° in a zirconia crucible for 8–12 hr. The melt was cooled slowly at a rate of 100° per hour. The sample was then treated by the same procedure described for α-AlB_{12}. The two phases could not be separated further because the crystals were intergrown. The best sample was estimated by intensities of X-ray diffraction lines to contain at least 90% of γ-AlB_{12} (40% yield).

Anal. Calcd. for AlB_{12}: Al, 17.19; B, 82.81. Found: Al, 17.01; B, 82.30.

$C_2Al_3B_{48}$ (β-AlB_{12}).—This phase was prepared by fusing a mixture of 300 g. of aluminum, 15 g. of boron, and 0.50 g. of carbon at 1400° in a zirconia crucible for 8 hr. and subsequently cooling at a rate of 100° per hour. Excess aluminum was removed by treatment with hydrochloric acid and the +20 mesh fraction was separated. This fraction consisted of a mixture of several phases and the amber crystals of $C_2Al_3B_{48}$ were hand-picked under a magnifying glass and a binocular microscope (3% yield). About 25 g. of the $C_2Al_3B_{48}$ was collected from a series of runs.

Anal. Calcd. for $C_2Al_3B_{48}$: Al, 12.96; B, 83.20; C, 3.84. Found: Al, 13.05; B, 83.35; C, 3.00.

C_4AlB_{24} (AlB_{10}).—This material was prepared by fusing a mixture of 400 g. of aluminum and 20 g. of boron in a graphite crucible at 1400° for 6 hr. Carbon must be added to the mixture when a graphite crucible is not used. The sample after removal of excess aluminum consisted of a black and a yellow phase. The yellow phase was removed by treatment with nitric acid. The remaining black phase (50% yield) corresponded crystallographically to that described for AlB_{10}. The density was found to vary between 2.48 and 2.57 g./cc. This composition was found to be independent of the amount of carbon added to the original mixture.

Anal. Calcd. for C_4AlB_{24}: Al, 8.06; B, 77.59; C, 14.35. Found: Al, 7.91; B, 77.34; C, 14.05.

$Al_4C_4B_{1-3}$.—In the preparation of C_4AlB_{24} a yellow phase which decomposes in nitric acid was observed as described above. Crystals of this phase were hand-picked and examined by chemical analysis and X-ray diffraction methods. The boron content was found to vary from 6 to 14%.

Anal. Calcd. for Al_4C_4B: Al, 64.71; B, 6.49. C, 28.80; Found: Al, 63.71; B, 8.34; C, 27.60.

Comments on the Crystallography of C_4AlB_{24} and $C_2Al_3B_{48}$.—A determination of structures of C_4AlB_{24} and $C_2Al_3B_{48}$ has been undertaken in this laboratory and is still in progress. The preliminary results are, however, pertinent to the subject of this study and a short summary of the information obtained to date is given below.

A. On the Structure of the C_4AlB_{24}.—On the basis of systematic extinctions the space group of C_4AlB_{24} is either $B2/b2_1/m$-$2/m$ or $Bb2_1m$ and the cell dimensions are a = 8.88 Å., b = 9.10 Å., and c = 5.69 Å. as previously reported.[6] There are two formula units per unit cell. The Patterson projection $P(xy)$ was computed and was found to be consistent with four B_{12} icosahedra in position 4C of the $B2/b2_1/m2/m$ space group. This position has the symmetry 2mm with one variable parameter. Because projection $P(xy)$ allows for two possible parameter values, *i.e.*, 0.10 or 0.15 (fractional coordinates), the latter was uniquely determined by computation of the three-dimensional Patterson map. Electron density maps were computed on (001) and (010) planes. These revealed the carbon positions.

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(13) V. I. Matkovich, *J. Am. Chem. Soc.*, **83**, 1804 (1961).

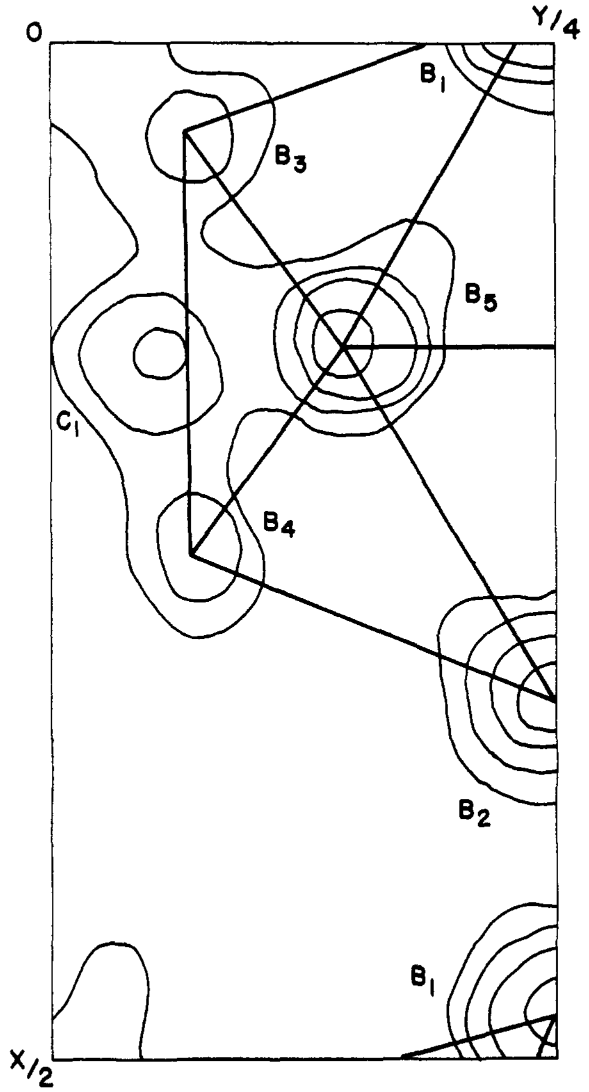

Fig. 1.—Electron density projection onto (001) of C_4AlB_{24}. The contour lines are drawn at arbitrary intervals with the first one at the zero level.

Least-squares refinement of carbon and boron atoms yielded an *R*-factor of 0.17 (observed reflections only).

Difference maps were then computed for both projections in order to place the aluminum atoms. These proved to be inconclusive which probably means that the aluminum is distributed over several sites in the structure, none of which is sufficiently strong to show on the difference map. Thus, one may consider this compound as a boron carbide with a small amount of aluminum as illustrated by expressing the formula as $B_6CAl_{0.25}$. It is possible that a three-dimensional refinement may show the aluminum more clearly.

It is interesting to note that the electron density map shown here (Fig. 1) is almost identical with the one published by Will.[10] Will's map is based on an icosahedral parameter of 0.10, the other choice in P(xy). This similarity is due to the twofold ambiguity in this projection.

The intericosahedral bonding in this structure is quite interesting. In the z-axis direction, the icosahedra are bonded into infinite chains by the carbon atoms. Two equivalent borons in adjacent icosahedra are joined to the same carbon atom in a nonlinear B–C–B arrangement. There are two of these groups between pairs of icosahedra. In the directions perpendicular to z, the bonding is largely between borons in adjacent icosahedra. One set of bonds joins icosahedra at $z = 0$ and $z = {}^1/_2$ in the x-direction. The other set of bonds is approximately in the y-direction between icosahedra at the same level. The aluminum appears to fill vacancies in the structure and must play only a minor role in the bonding because of the low occupancy of atomic sites.

The structure is based on a hexagonal close packed arrangement of icosahedra. Lipscomb and Britton[14] predicted that such an arrangement would exist although they were thinking in terms of boron only. Their predicted cell dimensions are quite close to those observed in C_4AlB_{24} and the space group is the same.

The atomic parameters are listed in Table III.

Table III

Atomic Parameters for C_4AlB_{24}

Atom	Equipment	x	y	z
B_1	8g	−0.014	0.250	0.167
B_2	8g	.318	.250	0.167
B_3	8f	.044	.084	0
B_4	8f	.246	.092	0
B_5	16h	.147	.150	0.250
C_1	8g	.157	.061	0.500

B. On the Unit Cell of the $C_2Al_3B_{48}$ (β-AlB_{12}).—The discussion of this material up to this point has been based on the presumption of a single phase as reported in the literature. While these data are adequate for the identification of the material it was noticed during the X-ray examinations that observed systematic extinctions exceeded considerably the requirements of the specified space group. A closer examination resolved this problem in a most surprising way. It was found that $C_2Al_3B_{48}$ is not a single compound at room temperature but consists of two crystallographically related phases which are formed by disproportionation of a single high temperature phase.

This high temperature phase was found to be tetragonal with $a = 8.82$ Å. and $c = 5.09$ Å. at about 850° (with P4/nmm or P4/n space group). The composition $C_2Al_3B_{48}$ can therefore only be assigned to this high temperature phase and the unit cell contains one molecule of $C_2Al_3B_{48}$. A high temperature X-ray camera purchased from Materials Research Corp. was used for this determination.

On cooling, the high temperature phase disproportionates into two related phases of different composition which are always present in the same relative proportions. Both phases are orthorhombic. The unit cell of one phase is $a = 12.34$ Å., $b = 12.63$ Å., and $c = 5.08$ Å. (space group: Cmma or C2ma). The unit cell of the other phase is $a = 6.17$ Å., $b = 12.63$ Å., and $c = 10.16$ Å. (space group: Ammm, A222, or A2mm). The dimensional similarity of the two phases permits their intertwinning and enables the specimens at room temperature to retain the form of the high temperature crystal. The composition of these two phases has not been established.

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(14) W. N. Lipscomb and D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).