

pyramid. The shortest  $N^+ \cdots Br^-$  distance is 3.17 Å, slightly longer than that in capaurine hydrobromide as shown in Fig. 11(a) in which the bromide ion occupies a site on the line  $N^+-H \cdots Br^-$  as (c). The second nearest approach is 3.90 Å. The spatial relationship of the halide anion to the nitrogen in the present crystal is rather similar to that observed in tetravalent  $(R)_4N^+$  ions (d) (Fridrichsons & Mathieson, 1963).

Fairly strong hydrogen bonds,  $O-H \cdots O$ , are observed, as indicated by dashed lines in Fig. 9, with the  $O \cdots O$  distances of 2.76 and 2.66 Å, the angles  $C-O \cdots O$  being 127.6 and 130.9° respectively. The distances between  $O(W)$  and  $Br^-$  were found to be 3.28 and 3.39 Å, and that between  $O(W)$  and  $O(4)$ , 3.09 Å. These distances are reasonable for the forma-

tion of a hydrogen bond. The presence of the molecules of water appears to be essential for stability.

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## Structure of $MgAlB_{14}$ and a Brief Critique of Structural Relationships in Higher Borides

BY V. I. MATKOVICH AND J. ECONOMY

*Research Branch, The Carborundum Company, P. O. Box 337, Niagara Falls, New York 14302, U.S.A.*

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A new boride of approximate composition of  $MgAlB_{14}$  has been prepared and the structure determined. The unit cell is orthorhombic  $a = 10.313$ ,  $b = 8.115$ ,  $c = 5.848$  Å, space group = *Imam*. Four icosahedral  $B_{12}$  groups centered at  $000$ ,  $0\frac{1}{2}\frac{1}{2}$ ,  $\frac{1}{2}00$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  are present. The icosahedra are oriented in such a way that two of the apical atoms lie along the  $a$  axis and a mirror plane of the icosahedra lies in the  $ab$  plane. The aluminum atoms occupy a fourfold position at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  and magnesium occupies a fourfold position at  $\frac{1}{2}y0$  ( $y = 0.359$ ). Partial occupancy is indicated for both metal atoms. The extra icosahedral boron atoms occupy the eightfold position at  $xy0$  ( $x = 0.152$  and  $y = 0.622$ ). Forty boron atoms have six boron and two metal neighbors. Eight boron atoms have six boron neighbors, and eight (extra icosahedral) boron atoms have four boron and three metal neighbors. Aluminum has twelve and magnesium has fourteen neighbors. The  $B_{12}$  icosahedral units in  $MgAlB_{14}$  are arranged in somewhat distorted closest packed layers which are stacked directly one above the other. This new arrangement of  $B_{12}$  units (which is denoted as 4HPo) conforms with the concept of packing models which can be derived by stacking of closest packed layers. It is shown how analysis of unit-cell dimensions and symmetry based on this concept greatly simplified the structure determination. The predictive nature of directional external icosahedral bonding is discussed in light of the tendency of  $B_{12}$  borides to form closest packed arrangements. It is shown that flexibility of bonding and presence of interstitial atoms permits a great variety of relative orientations of icosahedra. This observation justifies the use of a quasi-spherical  $B_{12}$  model where the three-dimensional framework is built by stacking of closest packed layers of  $B_{12}$  units.

### Introduction

From the time that the icosahedral boron groups were first established in boron carbide by Zhdanov & Sevastyanov (1941) a number of refractory borides have been found to contain  $B_{12}$  polyhedral units in various arrangements. Among these are tetragonal boron (Hoard, Hughes & Sands, 1958), simple rhombohedral boron (Decker & Kasper, 1959), rhombohedral boron phosphides and silicides (Matkovich, 1960, 1961a), rhombohedral boron oxide and arsenide (La Placa & Post, 1961),  $C_4AlB_{24}$  (Matkovich, Economy & Giese, 1964),  $AlB_{10}$  (Will, 1967),  $BeB_{12}$  (Becker, 1960),  $B_{12}C_2Al$  (Economy, Matkovich & Giese, 1965), com-

plex rhombohedral boron (Hughes, Kennard, Sul-lenger, Weaklien, Sands & Hoard, 1963) and  $YB_{70}$  (Richards & Kasper, 1965). Derivative similarities between various higher borides were first reported by Matkovich (1961b) who noted that compounds of different stoichiometries may be derived from the same icosahedral framework and that differences are due to substitution or degree of occupancy of extra-icosahedral atoms in interstitial holes. A few isotopic series that can be explained in this manner are frequently referred to as derivatives of known boron modifications (Giese, Economy & Matkovich, 1965; Economy, Matkovich & Giese, 1965). A more general observation as to arrangement of icosahedra in the  $B_{12}$

borides was reported by Matkovich, Giese & Economy (1965). They found that in all known refractory  $B_{12}$  borides the polyhedral units tend to form closest packed layers and that three features differentiate these structures, namely, (1) type of polyhedral unit, (2) manner of stacking of closest packed layers, and (3) presence of interstitial atoms.

The packing concept is particularly useful in predicting arrangements of polyhedral units from simple dimensional analysis of the unit cell. This has been used to great advantage in the structure determination of  $MgAlB_{14}$ , which is reported here for the first time. An attempt is also made to bring into focus apparent inconsistencies between the concept of packing and the directional extra-icosahedral bonding of the  $B_{12}$  unit. The role of interstitial atoms in such structures is also considered.

### Experimental

Crystals of  $MgAlB_{14}$  were initially isolated in small concentrations from a mixture of aluminum borides which was prepared by heating boron and aluminum to 1000–1400°C. Magnesium is present as an impurity in the boron used in the experiments. Larger amounts of the  $MgAlB_{14}$  crystals could be prepared by heating a mixture of magnesium, boron and aluminum in atomic proportions of 1:2:14. The mixture was heated to 900°C for six hours, cooled and treated with concentrated hydrochloric acid. A residue of small black crystals was isolated and shown to be a single phase of approximate composition  $MgAlB_{14}$ . A typical chemical analysis was:

Theoretical for $MgAlB_{14}$ :	Mg, 11.99%; Al, 13.31%;
	B, 74.70%
Found:	Mg, 10.04%; Al, 14.84%;
	B, 73.83%

Samples were found to contain up to 1% nitrogen which was most likely present as AlN. The total metal content was often lower than the indicated stoichiometry and the Al/Mg atomic ratio was in all cases found to be larger than one. The lowest magnesium content observed was about 6% (about half of the stoichiometric value). The density, measured by pycnometer, varied from 2.60 to 2.68 g.cm<sup>-3</sup>.

A small crystal suitable for X-ray measurements was selected and a preliminary examination made by use of Weissenberg photographs. These showed that the unit cell is orthorhombic with cell dimensions  $a=10.313$ ,  $b=8.115$  and  $c=5.848$  Å. All reflections were consistent with the requirements  $h+k+l=2n$  and the  $h0l$  reflections where  $h$  or  $l$  are odd were absent; these conditions are consistent with  $Imam$  or  $Ima2$  space groups. From the unit-cell dimensions and the density the sum of atomic weights per lattice point is between 191.5 and 197.5, compared with the theoretical sum of atomic weights of 202.63 for the formula  $MgAlB_{14}$ . The selected crystal had a density of about 2.60 g.cm<sup>-3</sup>. Crystals of higher density were isolated but were too small for handling.

X-ray measurements were obtained with a General Electric XRD-5 unit (stationary-counter, stationary-crystal arrangement) with copper radiation and balanced nickel and cobalt filters. The intensity was taken proportional to the number of counts with the nickel filter minus the number of counts with the cobalt filter. Lorentz and polarization corrections were made in the usual manner. No absorption corrections were applied. The atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1962). A block-diagonal least-squares refinement was used which minimizes the function  $\sum_{hkl} w(K^2 F_o^2 - F_c^2)^2$ . All

reflections were given a weight of unity. The three-dimensional electron density maps were computed with an IBM 7090 computer using an *ERFR-2* program (Sly, Shoemaker & van den Hende, 1962).

The structure analysis of  $MgAlB_{14}$  was approached by assuming that the boron atoms form  $B_{12}$  icosahedral groups and that a three-dimensional network is formed by stacking of the closest packed layers of  $B_{12}$  units. This method of analysis is discussed in an earlier paper (Matkovich, Giese & Economy, 1965) while specific application to  $MgAlB_{14}$  is described later in this paper (see Fig. 2). As shown in Fig. 2, analysis of the unit-cell dimensions in view of space group requirements and average icosahedral diameter of 5.1 Å indicates that the closest packed layers of  $B_{12}$  groups are stacked directly above one another along the  $a$  axis, and that each layer contains  $B_{12}$  groups of two different orientations. The space group  $Imam$  was assumed since it is consistent with this arrangement. The symmetry of the space group requires that the mirror plane of the icosahedra lie in the  $ab$  plane.

A three-dimensional Patterson map was computed and was found to be consistent with the orientation of icosahedra where two apical boron atoms lie approximately along the  $a$  axis and additional atoms are present in  $4(d)$  or  $4(c)$  positions at either  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$  or  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$  (depending upon the relative orientation of icosahedra which are centered at  $000$ ,  $0\frac{1}{2}\frac{1}{2}$ ,  $\frac{1}{2}00$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ). After placing the 48 boron atoms in an approximate icosahedral arrangement (32 atoms in  $16(j)$  positions and 16 atoms in  $8(h)$  positions) and four aluminum atoms in the  $4(d)$  positions, five cycles of least-squares refinement were carried out and a three-dimensional electron density map was computed. At this point the  $R$  value, which is defined as

$$R = \frac{\sum(|KF_o| - |F_c|)}{\sum|KF_o|},$$

was 0.30 and the electron density map indicated presence of four additional metal atoms (magnesium) in the  $4(e)$  position (at  $\frac{1}{4}y0$ ) and eight additional boron atoms in the  $8(h)$  position (at  $xy0$ ). Thus, all the atoms were accounted for and their positions are illustrated in Fig. 1. Subsequent least-squares refinement including all atoms reduced the  $R$  value to about 0.15. It became obvious, however, that the temperature factor for the magnesium position was too high, which was in agree-

ment with the observed deficiency of magnesium in the compound. Various combinations of the metal occupancies were then tried; the best agreement was obtained for a composition of  $Mg_{0.5}AlB_{14}$  where about one quarter of aluminum is randomly distributed among magnesium positions. At this point the  $R$  value was 0.12. The temperature factor for magnesium is still significantly higher than that for the other elements in the structure; it can be reduced by further lowering the Mg occupancy, but this results in an increase in the  $R$  value. To reconcile the structural results with the chemical analysis and density one must assume that both metals have partial occupancy and that some aluminum atoms are randomly distributed among the magnesium positions.

Table 1 gives a list of atomic parameters; Table 2 gives a list of interatomic distances; and Tables 3 and 4 give the crystal data and a list of calculated and observed  $F$  values respectively.

As can be seen from Fig. 1, 40 boron atoms have six boron and two metal neighbors. Eight boron atoms have six boron neighbors, and eight (extra-icosahedral) boron atoms have four boron and three metal neighbors. Aluminum has 12 and magnesium has 14 boron neighbors.

### Discussion

#### Structure of $MgAlB_{14}$

The atomic arrangement of  $MgAlB_{14}$  has been determined and the structure shown to be related to other

higher borides which are based on simple arrangements of icosahedral boron groups. The intraicosahedral boron-boron distances range from 1.79 to 1.84 Å with an average of 1.810 Å. These values are in good agreement with distances observed in icosahedral groups of other higher borides. Similarly, as in most of the other  $B_{12}$  borides, the external boron-boron distances are shorter and average 1.761 Å. The two extra-icosahedral boron atoms are at a somewhat larger distance of 2.040 Å. Magnesium has 12 bonds to boron atoms in six different icosahedra at an average distance of 2.730 Å and two bonds to extra-icosahedral boron neighbors at a distance of 2.363 Å. These values may be compared with the sum of the radii of magnesium and boron of 2.50 Å (observed in  $MgB_2$  by Russell, Hirst, Kanda & King, 1953). Aluminum has eight bonds to atoms in four different icosahedra at an average distance of 2.37 Å [which agrees very well with the sum of radii values of 2.40 Å observed in  $AlB_2$  by Felten (1956)] and four extra-icosahedral boron atoms at a short distance of 2.061 Å.

The structure of  $MgAlB_{14}$  is based on a simple hexagonal arrangement of icosahedra where orientation of icosahedral groups requires orthorhombic symmetry. Using the method of classification mentioned earlier (Matkovich, Giese & Economy, 1965),  $MgAlB_{14}$  can be regarded as a derivative of a packed model designated as 4HP $o$  where HP denotes hexagonal primitive arrangement of icosahedra,  $o$  denotes the orthorhombic symmetry and 4 shows that the ortho-

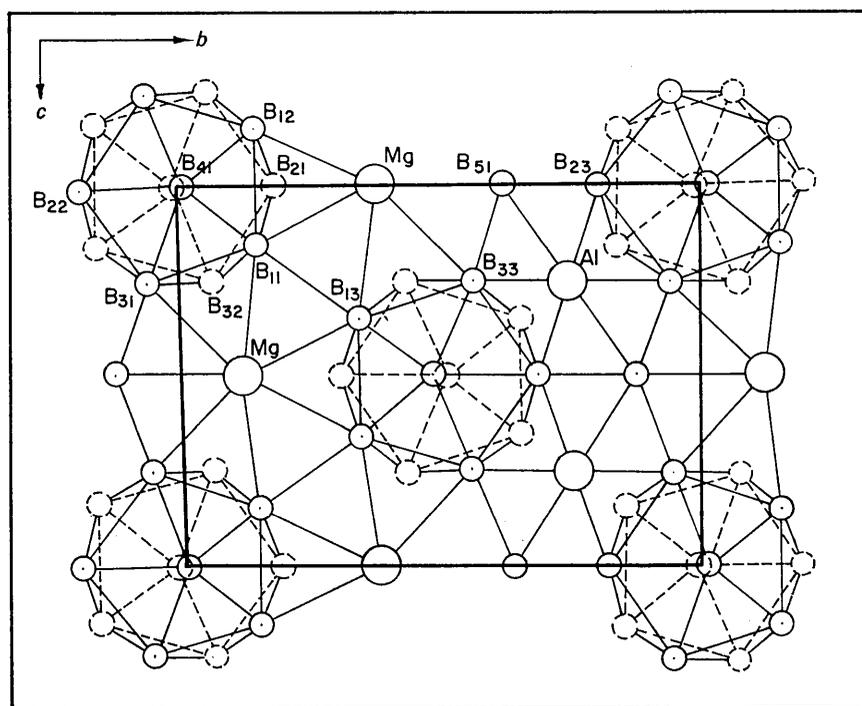


Fig. 1. A layer of icosahedra in  $MgAlB_{14}$  with extra-icosahedral atoms. The atoms shown fall within  $x = \pm \frac{1}{4}$ .

rhombic cell is four times larger than the basic HP model. Classification of  $\text{MgAlB}_{14}$  in this manner is particularly useful because of variable occupancy in the interstitial positions and the possibility that such atoms may be substituted by others.

#### Approach to structure analysis

The structure determination was greatly facilitated by use of the packing concept which is based on the observation that in all icosahedral structures the polyhedral units form approximate closest packed layers. The possible three-dimensional arrangements of units can be easily derived by examination of the various ways in which such layers can be stacked (Matkovich & Economy, 1968). Comparison of dimensional relationships of these arrangements with the information of the unit-cell dimensions, symmetry requirements, density of the crystal and chemical analysis can lead to a correct placement of polyhedral units even before the structure determination is undertaken. The interstitial or extra-icosahedral atoms can then be positioned by computation of the electron density maps.

As hexagonal layers consist of equilateral triangles, a simple distortion is represented by the elongation of

one of the triangular sides. It can be readily seen (Fig. 2) that the  $b$  and  $c$  axis dimensions of the unit cell of  $\text{MgAlB}_{14}$  can be derived by such a distortion of the closest packed layers of spheres of about  $5.1 \text{ \AA}$  diameter. Thus, assuming the presence of the  $\text{B}_{12}$  units, the  $b$  and  $c$  axis dimensions suggest that the  $a$  face is centered by a  $\text{B}_{12}$  group oriented differently than the one in the origin. The observed body centering requires that there be two such layers per unit cell and that the layers be stacked directly one above the other along the  $a$  axis. As the  $\text{B}_{12}$  icosahedral group has an average diameter of  $5.1 \text{ \AA}$ , this type of stacking is in good agreement with the observed  $a$  axis length of  $10.313 \text{ \AA}$ . Thus the four icosahedral groups in the unit cell account for 48 boron atoms, leaving eight boron and eight metal atoms to be placed in the interstitial openings among the  $\text{B}_{12}$  groups.

It is important to note that the interstitial atoms were disregarded in this consideration. This approach is justified as the above analysis is based on the observation that the diameter of the polyhedra is so much greater than that of single atoms that their presence results in only minor changes in the interpolyhedral distances.

Table 1. List of atomic parameters

Equivalent position	Occupancy number	Type of atom	$x$	$y$	$z$	$B$
4( $d$ )	$\sim 3$	Al	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$	0.172
4( $e$ )	$\sim 1$	Al	$\frac{1}{4}$	0.359	0	1.205
4( $e$ )	$\sim 2$	Mg				
16( $j$ )	16	B(1)	0.063	0.164	0.158	0.070
8( $h$ )	8	B(2)	0.086	-0.173	0	0.103
16( $j$ )	16	B(3)	0.080	-0.045	0.250	0.070
8( $h$ )	8	B(4)	0.167	0.029	0	0.043
8( $h$ )	8	B(5)	0.152	0.622	0	0.063

The standard deviations are  $\pm 0.0007$  for  $x$ ,  $\pm 0.009$  for  $y$ ,  $\pm 0.001$  for  $z$  and  $\pm 0.095$  for  $B$ .

Table 2. Interatomic distances

Intra-icosahedral bonds		Extra-icosahedral bonds	
B(4) <sub>1</sub> -B(1) <sub>1</sub>	1.788 $\pm$ 0.017 $\text{\AA}$	B(4) <sub>1</sub> -B(4) <sub>2</sub>	1.751 $\pm$ 0.014 $\text{\AA}$
B(4) <sub>1</sub> -B(3) <sub>1</sub>	1.809 $\pm$ 0.013	B(1) <sub>1</sub> -B(1) <sub>3</sub>	1.752 $\pm$ 0.015
B(4) <sub>1</sub> -B(2) <sub>2</sub>	1.835 $\pm$ 0.015	B(2) <sub>3</sub> -B(5) <sub>1</sub>	1.787 $\pm$ 0.016
B(2) <sub>1</sub> -B(1) <sub>1</sub>	1.787 $\pm$ 0.013	B(3) <sub>3</sub> -B(5) <sub>1</sub>	1.755 $\pm$ 0.017
B(2) <sub>1</sub> -B(3) <sub>2</sub>	1.798 $\pm$ 0.015	B(5) <sub>1</sub> -B(5) <sub>2</sub>	2.040 $\pm$ 0.014
B(1) <sub>1</sub> -B(3) <sub>1</sub>	1.791 $\pm$ 0.015	B(1) <sub>1</sub> -Mg	2.666 $\pm$ 0.017
B(1) <sub>1</sub> -B(3) <sub>2</sub>	1.837 $\pm$ 0.017	B(1) <sub>3</sub> -Mg	2.787 $\pm$ 0.007
B(1) <sub>1</sub> -B(1) <sub>2</sub>	1.853 $\pm$ 0.012	B(3) <sub>3</sub> -Mg	2.736 $\pm$ 0.017
B(3) <sub>1</sub> -B(3) <sub>2</sub>	1.793 $\pm$ 0.016	B(5) <sub>1</sub> -Mg	2.363 $\pm$ 0.016
		B(3) <sub>3</sub> -Al	2.422 $\pm$ 0.008
		B(2) <sub>3</sub> -Al	2.324 $\pm$ 0.008
		B(5) <sub>1</sub> -Al	2.061 $\pm$ 0.008

Table 3. Crystal data

Composition	Theoretical $\text{MgAlB}_{14}$	Found $\text{Mg}_{0.5-0.8}\text{Al}_{1.0-1.1}\text{B}_{14}$
Formula weight	Theoretical 202.78	Found 191.5-197.5
Density	Theoretical 2.75 $\text{g.cm}^{-3}$	Found 2.60-2.68 $\text{g.cm}^{-3}$
Unit-cell dimensions	$a = 10.313$ , $b = 8.115$ , $c = 5.848 \text{ \AA}$	
Space group	$Im\bar{m}$	

Table 4. Observed and calculated structure factors

h	k	F <sub>obs</sub>	F <sub>calc</sub>	h	k	F <sub>obs</sub>	F <sub>calc</sub>	h	k	F <sub>obs</sub>	F <sub>calc</sub>
$\ell = 0$											
2	0	3.76	6.64	3	8	11.54	-10.01	0	0	80.30	91.41
4	4	8.92	-6.84	5	8	8.67	6.76	2	0	33.34	-40.83
6	0	86.00	-83.83	7	8	21.40	-22.63	4	0	5.35	-2.48
8	0	8.82	-17.93	0	9	30.15	-31.83	6	0	30.77	-31.80
10	0	54.92	-46.75	2	9	13.22	-11.13	8	0	16.49	19.22
12	0	77.93	70.35	4	9	15.16	14.41	10	0	12.94	-12.49
1	1	26.39	26.06	1	10	12.07	-15.81	1	1	32.67	30.00
3	1	7.33	-6.91	0	0	2.28	2.70	3	1	23.33	30.03
5	1	21.65	-18.53	2	0	43.25	-41.53	5	1	26.25	23.34
7	1	25.61	-25.97	4	0	22.28	-19.89	7	1	13.55	-9.90
9	1	4.54	4.44	6	0	51.67	53.73	9	1	6.45	-8.65
11	1	2.20	-1.02	8	0	16.25	14.27	0	2	14.89	15.35
0	2	4.18	-2.06	10	0	6.46	-6.66	2	2	29.79	31.17
2	2	23.37	20.56	12	0	1.68	-0.08	4	2	31.26	-33.66
4	2	50.03	-47.35	1	1	26.27	-26.44	6	2	12.91	11.74
6	2	34.83	33.74	3	1	62.23	64.32	8	2	41.17	-39.14
8	2	28.65	-26.21	5	1	36.55	-34.85	10	2	5.07	5.36
10	2	25.65	21.48	7	1	34.78	31.90	1	3	13.66	-14.51
12	2	6.25	8.18	9	1	31.07	-26.51	3	3	44.57	46.62
1	3	21.72	-20.02	11	1	13.72	9.30	5	3	13.66	-15.34
3	3	64.52	65.62	0	2	32.95	32.51	7	3	16.43	12.25
5	3	27.15	-24.30	2	2	47.29	-46.76	9	3	25.95	-26.16
7	3	19.93	16.96	4	2	27.95	27.58	0	4	23.75	18.48
9	3	35.68	-31.43	6	2	22.22	24.92	2	4	3.18	4.45
11	3	9.40	5.42	8	2	22.58	20.22	4	4	12.26	8.38
0	4	16.22	-11.70	10	2	35.59	-33.04	6	4	22.65	-18.87
2	4	12.88	-13.78	12	2	1.51	-2.32	8	4	13.58	-13.91
4	4	5.70	8.28	1	3	3.33	3.25	1	5	11.90	14.80
6	4	1.44	-0.09	3	3	36.52	-35.82	3	5	5.57	-28.11
8	4	4.90	7.15	5	3	4.00	-4.40	5	5	35.04	36.59
10	4	13.64	10.66	7	3	7.02	-5.01	7	5	39.27	-40.37
1	5	44.35	41.16	9	3	38.95	36.17	0	6	14.30	10.14
3	5	3.19	2.18	11	3	1.84	-0.51	2	6	2.28	-0.61
5	5	83.45	85.14	0	4	55.46	-55.87	4	6	17.24	-15.37
7	5	39.97	-35.56	2	4	32.95	32.51	6	6	16.98	12.25
9	5	2.20	-4.29	4	4	23.54	-21.98	1	7	8.22	-9.81
11	5	36.43	-35.68	6	4	45.31	41.45	3	7	52.33	52.97
0	6	33.10	31.66	8	4	35.01	-30.78	5	7	34.23	32.87
2	6	28.62	31.47	10	4	22.80	18.66	0	8	10.68	13.71
4	6	12.92	-17.82	1	5	41.61	-44.20	2	8	25.58	-28.98
6	6	15.67	-12.23	3	5	44.50	-44.57				
8	6	37.81	37.30	5	5	14.83	-15.39				
10	6	4.03	-2.06	7	5	4.35	5.62				
1	7	26.82	-26.09	9	5	26.45	23.08				
3	7	30.75	29.54	0	6	38.67	37.05				
5	7	6.34	4.71	2	6	28.83	-28.34				
7	7	22.08	-21.49	4	6	16.40	14.35				
9	7	37.96	-41.24	6	6	27.89	-25.31				
0	8	4.92	3.06	8	6	20.65	19.01				
2	8	47.95	-46.43	1	7	4.92	-2.86				
$\ell = 1$											
4	8	24.68	23.11	3	7	22.85	-22.94				
6	8	20.06	20.39	5	7	34.99	34.27				
1	9	3.31	2.86	7	7	21.96	-22.79				
3	9	7.30	2.14	0	8	18.58	15.25				
5	9	5.23	11.25	2	8	7.56	9.87				
0	10	48.95	-53.82	4	8	17.89	-18.86				
2	10	3.36	-2.60	6	8	7.56	9.55				
4	1	22.17	22.14	1	9	34.33	-33.50				
2	1	29.10	27.00	3	9	7.41	7.24				
4	1	19.51	-18.58	0	1	17.15	-18.05				
6	1	6.15	4.41	2	1	3.18	0.41				
8	1	28.02	-27.52	4	1	13.96	-14.39				
10	1	10.36	8.33	6	1	18.61	18.04				
12	1	6.63	7.53	8	1	5.68	-5.03				
1	2	2.55	-1.61	10	1	21.69	19.68				
3	2	33.78	-30.50	1	2	15.95	19.07				
5	2	35.89	32.03	3	2	18.92	14.87				
7	2	38.91	-37.38	5	2	56.45	60.75				
9	2	1.63	-2.74	7	2	17.95	-19.70				
11	2	8.32	12.28	9	2	19.81	-16.74				
0	3	11.05	8.92	11	2	14.74	-14.81				
2	3	59.55	-57.21	0	3	52.66	54.90				
4	3	13.30	11.63	2	3	11.08	-11.58				
6	3	26.37	30.49	4	3	9.48	8.63				
8	3	30.99	26.70	6	3	2.74	0.79				
10	3	24.15	-20.45	8	3	13.87	-13.32				
12	3	9.19	8.33	10	3	45.56	-42.19				
1	4	24.72	-21.89	1	4	27.24	-31.49				
3	4	7.87	5.73	3	4	29.06	-27.61				
5	4	6.67	9.41	5	4	19.37	-21.01				
7	4	10.96	9.33	7	4	6.96	-3.53				
9	4	2.29	1.48	9	4	15.62	13.17				
11	4	6.16	4.23	0	5	18.86	20.45				
0	5	41.89	43.69	2	5	13.18	-15.25				
2	5	5.44	-3.90	4	5	15.32	-13.06				
4	5	12.16	-13.78	6	5	14.66	12.06				
6	5	4.20	0.71	8	5	6.27	7.90				
8	5	6.31	-7.05	1	6	11.38	-9.13				
10	5	14.51	-13.42	3	6	16.76	13.80				
1	6	11.53	-10.03	5	6	15.53	-11.94				
3	6	21.04	19.81	7	6	3.24	0.29				
5	6	12.35	-10.66	2	7	2.28	2.28				
7	6	4.59	2.79	7	7	23.55	-25.19				
9	6	3.37	-1.72	4	7	4.66	7.53				
0	7	8.64	-5.00	6	7	10.15	12.91				
2	7	25.25	20.37	1	8	13.57	10.28				
4	7	14.05	-9.58	3	8	18.94	20.89				
6	7	3.54	0.64	5	8	34.36	34.19				
8	7	23.15	-19.33	0	9	1.62	2.24				
1	8	1.62	-1.32	2	9	13.64	12.39				
$\ell = 2$											
$\ell = 3$											
$\ell = 4$											
$\ell = 5$											
$\ell = 6$											
$\ell = 7$											

boron atoms display a pentagonal pyramidal coordination; the required coordination of 12 for the B<sub>12</sub> icosahedron may be obtained if the metal atoms are disregarded. The metal atoms in MgAlB<sub>14</sub> could be construed to act as electron donors to the B<sub>12</sub> icosahedra which, according to the Longuet-Higgins & Roberts (1955) model, possess a 2- charge. However, among the B<sub>12</sub> borides there are numerous deviations from this model which suggests a need for an improved understanding of the electronic nature of the B<sub>12</sub> groups.

#### Predictive properties of polyhedral borides

As discussed in the previous section, the tendency of B<sub>12</sub> icosahedral units to form closest packed layers which are stacked in different ways permits a certain degree of predictability for structure analysis. This approach greatly simplified the structure determination of MgAlB<sub>14</sub>. Another feature of the polyhedral B<sub>12</sub> unit is its tendency to form 12 external bonds whose directions coincide with the fivefold icosahedral axes. This property was used by Hughes *et al.* (1963) to derive the B<sub>84</sub> unit in  $\beta$  rhombohedral boron. The predictive utility of pentagonal pyramidal coordination has subsequently been discussed by Hoard & Hughes (1965, 1967).

It is worthwhile to examine the relative utility of these concepts more closely, since a cursory examination would indicate that these views are incompatible. Presumably, atoms (or groups of atoms) which display highly directed external bonding do not form closest packed layers, while atoms such as metals which form closest packed arrangements have a highly delocalized structure. In the B<sub>12</sub> borides a conflict exists only when extrapolyhedral or interstitial atoms are absent. In such a case each icosahedron may have 12 external

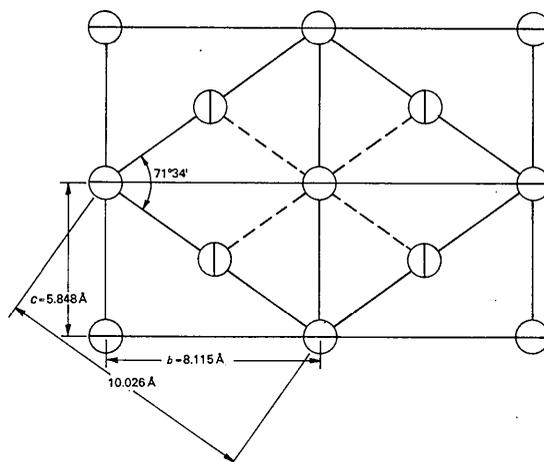


Fig. 2. Interpretation of unit-cell dimensions in terms of an icosahedral arrangement. The Figure illustrates how a distorted closest packed arrangement of B<sub>12</sub> units can be obtained by placing a differently oriented unit at the center of the *a* face.

In MgAlB<sub>14</sub> the B<sub>12</sub> icosahedron is in contact with 22 surrounding atoms (six of which belong to other icosahedra), and only one-sixth of the icosahedral

Table 5. *Pentagonal pyramidal coordination of icosahedral boron atoms*

Compound	Structure based on simple B <sub>12</sub> units	
	Number of icosahedra per unit cell	Number of icosahedral atoms with coordination of six
α-Boron (rhombohedral)	1	6
α-Boron derivatives (B <sub>4</sub> C, B <sub>6</sub> P, etc.)	1	12
Tetragonal boron (simple)	4	8
Tetragonal boron derivatives (BeB <sub>12</sub> , NiTaB <sub>24</sub> , etc.)	4	4-6
MgAlB <sub>14</sub>	4	2
C <sub>4</sub> AlB <sub>24</sub>	4	~10

bonds directed along the fivefold axes toward other icosahedra. Unfortunately, in this type of three-dimensional network, one is confronted with a framework which preserves fivefold symmetry axes and this is incompatible with lattice periodicity. Arrangements where a B<sub>12</sub> icosahedron is directionally bonded to 12 other B<sub>12</sub> icosahedra do occur. However, such grouping of icosahedra leads invariably to formation of larger polyhedral units (such as B<sub>84</sub> and B<sub>156</sub>) which do not display lattice periodicity. The periodicity of the crystalline lattice is always obtained by arrangement of polyhedral units into simple packing models.\*

When interstitial atoms are present in these structures there is then a possibility to satisfy the tendencies for the B<sub>12</sub> units to form close packed arrangements as well as highly directional external bonds. Yet, examination of Table 5 listing known structures based on simple B<sub>12</sub> units shows that the number of external icosahedral bonds which display pentagonal pyramidal coordination can range from two to twelve. From this observation one can only conclude that the B<sub>12</sub> unit has a high degree of flexibility in its external bonding. However there is still some tendency to form pentagonal pyramidal bonds and this feature may be used to a limited extent to predict orientation of icosahedral units and positions of interstitial atoms.

The view that emerges of the polyhedral borides is one where the directed boron bonds may be used in a predictive manner to derive complex polyhedral forms. The approximate three-dimensional arrangement of polyhedral units can be derived from models that can be obtained by stacking of closest packed layers of equal size spheres, and the orientation of units and placements of interstitial atoms tend to accommodate as many external directional bonds as possible.

\* The 156-atom unit observed in YB<sub>70</sub> (Richards & Kasper, 1965) should not be regarded as a quasi-sphere. These units are packed according to Kitaigorodski's (1955) rule which states that protrusions of one unit fit into cavities of the other yielding a higher density.

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