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The Crystal Structure of YB$_{66}$*

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The crystal structure of the compound YB$_{66}$ has been determined by single-crystal techniques utilizing X-ray intensities measured by a scintillation counter. The crystal system is cubic with $a = 23\cdot440$ ($\sigma = 0\cdot006$) Å; the space group is $Fm3c$ (O_h^5). There are approximately 1584 boron atoms and 24 yttrium atoms in the unit cell. The majority of the boron atoms (1248) are contained in thirteen-icosahedron units of 156 atoms each – a thirteen-icosahedron unit is a cluster of twelve B$_{12}$ icosahedra grouped around a thirteenth. Bonds connecting boron atoms within icosahedra range in length from $1\cdot719$ Å to $1\cdot855$ Å. The shortest intericosahedral bond is $1\cdot624$ Å; the longest is $1\cdot823$ Å. The remaining boron atoms are statistically distributed in channels that result from the packing of the thirteen-icosahedron units and form non-icosahedral cages. The yttrium atoms partially occupy sites in the channels and coordinate with the cage borons and the icosahedral borons surrounding them. The yttrium–boron bond lengths are in the range of $2\cdot691–2\cdot768$ Å.

Introduction

Among the large number of binary borides that are now known there occurs a variety of stoichiometries; and some metals, such as the rare-earths and yttrium, form an extensive series of borides. Thus, the following compounds are formed by yttrium: YB$_2$, YB$_4$, YB$_6$ and YB$_{12}$ (Post, 1964). The compound YB$_{12}$ is a representative of the phases with the highest boron to metal ratio that have been generally encountered. A phase with a much higher boron content, however, was discovered in 1958 by Seybolt (1960) during a study of boron-rich yttrium alloys. Its range of composition was found to be limited to only one to two atomic per cent yttrium. It was difficult to establish a precise formula for the compound and consequently the compound has been designated sometimes as YB$_{70}$ and sometimes as YB$_{100}$. As a result of our structure study, we believe the most appropriate formulation is YB$_{66}$.

Preliminary studies by one of us (J.S.K.) established that the compound was face-centered cubic with an approximate a of 23·5 Å.

Following Seybolt's discovery, other examples of this phase or similar phases with rare-earth metals or plutonium have been reported by various workers. A material described as YB$_{70}$ was tentatively assigned a tetragonal cell with $a = 11\cdot75$ Å, $c = 12\cdot62$ Å (Lundin, 1961). La Placa has prepared borides of Ho, Tb and Yb with approximate composition MB$_{70}$ that are face-centered cubic with $a = 23\cdot50$ Å (Post, 1964). Smith & Gilles (1964) have produced compounds which are considered to be YbB$_{100}$ and GdB$_{100}$ and which have diffraction patterns similar to YB$_{66}$. Eick (1965) has reported on the existence of the phase PuB$_{100}$.

All the substances cited above apparently have either the same structure as YB$_{66}$ or closely related structures, judging from the similarity of diffraction patterns. In the light of the complete structure analysis being reported here, it seems likely that all the compounds are similar in a major feature of the structure – the occurrence of a boron network resulting from the preservation of icosahedral packing to a high degree. It is quite possible, however, that in separate cases the ratio of metal atoms to boron atoms may vary. Further complete structure analyses would need to be done for

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* The major portion of this study was extracted from a thesis submitted by one of us (S.M.R.) to the Graduate School of Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry.

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the various compounds to establish whether they are very much the same in composition and structure as YB_{66} or whether they truly differ in composition and in the number of metal atoms per unit cell.

In all cases, other than YB_{66}, only polycrystalline material has been available. It would be practically impossible to solve the structure from powder diffraction patterns; as a matter of fact, even the indexing is somewhat tricky and erroneous reports of smaller unit cells have been made as a consequence. We were most fortunate to be provided by Dr A. U. Seybolt with single crystals of YB_{66} with which we could undertake a complete structure analysis of this interesting and important substance. The knowledge of the structure seemed desirable because of its probable pertinence to the structure of boron itself and also because of the interesting question as to how such an unusual stoichiometry comes about.

Experimental

Single crystals of YB_{66} appeared quite by accident in one of a series of melts of yttrium and boron prepared in a vacuum high-frequency induction furnace (Seybolt, 1960). The melt made with a nominal composition of 1·3 atomic per cent yttrium contained black, hard, friable little cubes of YB_{66} in combination with β-rhombohedral boron. An analysis of the Y content of the YB_{66} crystals gave the result $8·4 \pm 0·1\%$ by weight, or 1·1 atomic per cent yttrium. Although this percentage is considerably lower than the yttrium content of the crystal indicated by the structure determination (11·1%), the result is not entirely unexpected since in the process of selecting a sufficient quantity of material for analysis the inclusion of some β-rhombohedral boron was hard to avoid. The samples were examined by qualitative emission spectroscopy

Table 1. *Indexed powder pattern of* YB_{66}

		h	k	l	I*	d_{obs}	d_{calc}
		2	2	2	m	6·792	6·767
		4	0	0	s	5·880	5·860
		4	2	0	w+	5·248	5·241
		4	2	2	w	4·806	4·785
		4	4	0	vw	4·131	4·144
		5	3	1	s	3·945	3·962
		6	2	0	w	3·713	3·706
		6	2	2	vs	3·543	3·534
		6	4	0	w+	3·255	3·251
		6	4	2	vw	3·131	3·132
		7	3	1	vw	3·082	3·052
		8	0	0	vw	2·927	2·930
	6 4 4,	8	2	0	w+	2·843	2·843
	6 6 0,	8	2	2	m+	2·763	2·762
		7	5	1	w	2·703	2·707
		8	4	0	w	2·615	2·621
		7	5	3	m	2·574	2·573
		6	6	4	m+	2·500	2·499
		9	3	1	m	2·461	2·457
		8	4	4	m	2·397	2·392
	8 6 0,	10	0	0	s	2·347	2·344
	8 6 2,	10	2	0	s	2·301	2·299
		9	5	1	w	2·269	2·266
	8 6 4,	10	4	0	s+	2·176	2·176
		8	8	0	w	2·073	2·072
	8 8 2,	10	4	4	s−	2·042	2·040
	8 6 6,	10	6	0	m	2·012	2·010
		10	6	2	vw	1·982	1·981
	8 8 4,	12	0	0	w+	1·955	1·953
	10 6 4,	12	2	2	s	1·901	1·901
		12	4	0	m+	1·857	1·853
10 8 0,	8 8 6,	12	4	2	w	1·830	1·830
		10	8	2	vw	1·812	1·808
		10	6	6	m	1·788	1·787
	11 7 3,	13	3	1	w	1·754	1·752
		12	6	2	w	1·729	1·728
	11 7 5,	13	5	1	w−	1·680	1·679
10 10 0,	10 8 6,	14	2	0	vw	1·660	1·658
	11 9 1,	13	5	3	vw	1·643	⎰ 1·645
	14 2 2,	10	10	2			⎱ 1·641
		12	8	0	vw	1·627	1·625
	12 8 2,	14	4	0	w	1·611	1·610
12 6 6,	10 10 4,	14	4	2	w	1·595	1·595
		14	6	0	w	1·544	1·539

* Intensities: *vs*, strongest; *s+*, very strong; *s*, strong; *s−*, not quite so strong; *m+*, medium strong; *m*, medium; *w+*, medium weak; *w*, weak; *w−*, very weak; *vw*, weakest.

for impurities. Si was found to be present in trace quantities (10 p.p.m. or less). No test was made for C, N or O.

The cell constant was derived from Debye–Scherrer photographs of a fine powder of YB_{66}. The very rich powder pattern was readily indexed on the unit cell deduced from precession data for a single crystal. Selected high-angle lines were used to derive the cell constants by a combination of Nelson–Riley and least-squares procedures. The structure is face-centered cubic with $a = 23.440$, $\sigma = 0.006$ Å. The first 43 observed lines of the indexed powder pattern obtained with Ni-filtered Cu radiation are listed in Table 1. (The pattern contained additional lines from β-rhombohedral boron which formed along with the YB_{66}. These lines are not included in Table 1.) The experimental density of 2·52 g.cm^{-3} yields a value of 19,548 atomic weight units per unit cell, corresponding to 24·4 units of YB_{66}.

In addition to the systematic absences resulting from the face-centering condition, hhl reflections occur only if h and l are even. Within these restrictions two space groups are possible: the centrosymmetric $Fm3c$ and the non-centrosymmetric $F\bar{4}3c$. It was assumed that the space group was $Fm3c$, a choice which proved appropriate. It must be noted however, that some very small intensities were observed for a few of the hhl odd planes. Furthermore, on long exposure of the $l = 1$ layer, diffuse spots could be seen in the area of certain planes forbidden by the face centering condition. If these spots are other than artifacts it might be necessary to reassess the choice of space group; although even in this event the present structure undoubtedly represents a very close approximation to physical reality. These effects may be related to the systematic partial occupancy of certain sites.

Using Ni filtered Cu radiation, data were collected for two crystals. Both were mounted on the General Electric Company Single Crystal Orienter. The first set was collected manually by maximizing each reflection and measuring the peak height with a scintillation counter. The background was sampled on either side of the peak. 652 independent reflections were measured. The second set of data was collected with the Datex Automated System for the General Electric Orienter, using prepunched paper tape control. Peak height measurements (stationary counter method) were made for reflections with $2\theta \leq 90°$ and scanning techniques (θ–2θ) were used for reflections with $2\theta > 90°$. The intensities recorded from the two crystals showed good agreement; $\Sigma |I_1(hkl) - I_2(hkl)|/\Sigma I_1(hkl) = 0.05$. Both sets of data refined to essentially the same result; the parameters and structure factors derived from the manually collected data will be presented here. The crystal used was a slightly irregular parallelepiped of width 0·25 mm and length 0·41 mm.

The data were corrected for Lorentz and polarization factors and then for α_1–α_2 splitting by an empirical curve. No correction for absorption was made. (Even

at the maximum radius the value of the absorption correction would be very small since $\mu R = 0.3$).

Standard deviations (σ) were assigned to all reflections on the basis of statistical errors in the counts for peak (or integrated peak) and in the background counts. The inverse of the variance ($1/\sigma^2$) was used as the weighting factor for F^2 values in the refinement procedures.

The approximate solution of the structure resulted from a three-dimensional Patterson synthesis* coupled with structure factor calculations and crystal chemical considerations. The most outstanding peaks in the Patterson synthesis could only correspond to Y–Y vectors and after abortive attempts to assign yttrium to lower multiplicity positions in accordance with the reported chemical analysis, these peaks were satisfactorily interpreted as resulting from yttrium atoms in the 48(f) positions ($x\frac{1}{4}\frac{1}{4}$) with 50% occupancy. Many of the boron positions could then be obtained from the larger remaining peaks of the Patterson interpreted as Y–B vectors. Ambiguities or uncertainties about the remaining boron positions were resolved by utilizing information from known boron structures as to expected B–B distances and as to coordinations and geometry. A moderate amount of testing was required by means of structure factor calculations and Fourier synthesis, as well as compatibility with the Patterson map – to establish the 9 boron positions of the asymmetric unit which define the framework of the structure. This framework consists of an intricate arrangement of icosahedra which are for the most part bound to one another by bonds along the pseudo-fivefold axes. While the packing of icosahedra is quite dense, there do occur channels parallel to the fourfold axes at 48(f) positions ($x\frac{1}{4}\frac{1}{4}$), etc. The yttrium atoms occur in these channels along the fourfold axes.

Additional electron density was observed in the Fourier syntheses for regions in the channels surrounding the yttrium atoms. The peaks were quite close together and much lower in height than the framework borons (which were of uniform and appropriate height). After numerous attempts to derive models using these positions in configurations at full occupancy it was found necessary to assume that these atoms occupied these positions statistically and to introduce the occupancy factors into least-squares calculations as variables.† Four boron positions were treated in this manner. The final refinement procedures, by least squares, included anisotropic thermal parameters, using boron scattering factors from *International Tables* (Vol. III, 1962) and scattering factors for Y^{3+} (Cromer, Larson & Waber, 1964) corrected for anomalous dispersion. The final refinement converged to $R = \Sigma ||F_o|^2 - |F_c|^2|/\Sigma |F_o|^2$

$=0\cdot067$ (weighted $R=[\ \varSigma\ w(|F_o|^2-|F_c|^2)^2/\varSigma\ w(|F_o|^2)^2]^{1/2}$ $=0\cdot103$). The atomic coordinates, thermal parameters and occupancies, where relevant, are listed in Table 2. The observed and calculated structure factors are compiled in Table 3.

Discussion of the structure

General description

The YB$_{66}$ structure is basically an array of icosahedra grouped in clusters of thirteen in which twelve icosahedra are arranged (icosahedrally) around a central icosahedron. Eight of these 156 atom units are distributed within the unit cell and are interconnected through the external bonds of individual icosahedra. As a result of these interconnections an extensive framework is formed which contains empty channels along fourfold axes. The partially filled yttrium sites are found within these channels. At the junction of any three channels there are cage-like configurations of boron atoms bonded to the icosahedra surrounding them and providing additional coordination to the yttrium sites. The boron positions which make up these configurations are not completely filled. Al-

though one can obtain values for the occupancies of the sites from the least-squares refinement it is not possible to construct one single model in conformity with the occupancies without severe steric problems. In view of the statistical filling of the yttrium sites which surround the cages it seems not unlikely that more than one distinct configuration could exist in this area. In the following discussion the detailed construction of the framework and two configurations which may occur in the channels will be presented.

The icosahedral framework

The icosahedral framework is made up of 1248 boron atoms arranged in eight units of 156 atoms each. A convenient starting point for describing one of these units is the icosahedron which occurs about the origin of the unit cell as shown in Fig. 1. This icosahedron is oriented so that its three mutually perpendicular mirror planes are aligned perpendicular to the axes of the cube. Bonds radiating out from each atom along the fivefold axes of the central icosahedron lead to boron atoms of surrounding icosahedra. This thirteen-icosahedron unit may be generated by considering the central icosahedron to be reflected through planes per-

Table 2. *Atomic coordinates and thermal parameters*

Atom*	Fractional occupancy	Coordinates		
		x	y	z
1	0·5	0·05448 (5)	$\frac{1}{4}$	$\frac{1}{4}$
2	1·0	0	0·03716 (24)	0·05923 (24)
3	1·0	0	0·07598 (24)	0·11659 (25)
4	1·0	0	0·03889 (24)	0·18145 (23)
5	1·0	0	0·14835 (23)	0·24188 (24)
6	1·0	0	0·18593 (23)	0·17186 (24)
7	1·0	0·03845 (18)	0·14027 (16)	0·12163 (17)
8	1·0	0·03921 (19)	0·08171 (17)	0·22939 (16)
9	1·0	0·06306 (17)	0·07748 (17)	0·15860 (17)
10	1·0	0·06365 (18)	0·14595 (17)	0·19491 (19)
11	0·71 (2)	0·13193 (33)	0·17493 (35)	0·19719 (36)
12	0·65 (2)	0·23420 (53)	0·15866 (50)	0·30080 (62)
13	0·28 (2)	0·17343 (71)	0·12776 (64)	0·25728 (85)
14	0·279 (18)	0·23407 (82)	0·23407 (82)	0·23407 (82)

Anisotropic thermal parameters

Atom* number	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
1	0·00051 (2)	0·00048 (1)	0·00048 (1)	0	0	0
2	0·00038 (9)	0·00044 (9)	0·00039 (9)	0	0	−0·00009 (8)
3	0·00053 (10)	0·00041 (9)	0·00040 (10)	0	0	−0·00010 (8)
4	0·00048 (10)	0·00041 (9)	0·00029 (9)	0	0	−0·00004 (7)
5	0·00034 (8)	0·00035 (8)	0·00027 (10)	0	0	−0·00002 (7)
6	0·00045 (9)	0·00030 (9)	0·00040 (9)	0	0	0·00000 (8)
7	0·00068 (7)	0·00038 (6)	0·00038 (6)	0·00006 (6)	0·00009 (6)	0·00011 (5)
8	0·00068 (7)	0·00035 (6)	0·00031 (6)	−0·00001 (6)	−0·00006 (5)	0·00007 (5)
9	0·00045 (7)	0·00042 (7)	0·00050 (6)	−0·00002 (6)	0·00020 (5)	−0·00005 (5)
10	0·00052 (7)	0·00030 (7)	0·00076 (8)	0·00004 (5)	−0·00001 (6)	0·00005 (6)
11	0·00117 (16)	0·00140 (18)	0·00131 (20)	−0·00037 (12)	−0·00051 (12)	−0·00059 (15)
12	0·00215 (31)	0·00155 (25)	0·00359 (35)	−0·00027 (19)	−0·00056 (24)	0·00049 (24)
13	0·00101 (34)	0·00032 (28)	0·00111 (46)	−0·00014 (22)	−0·00084 (30)	0·00011 (27)
14	0·00130 (41)	0·00130 (41)	0·00130 (41)	0·00056 (24)	0·00056 (24)	0·00056 (24)

* Atom 1 is an yttrium atom; atoms 2–14 are boron.
The anisotropic temperature factor has the form $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$. Numbers in parentheses here are the estimated standard deviations in the least significant figures.

Table 3. *List of observed and calculated structure factors* $(x\frac{1}{4})$ *for* YB_{66}

$F(000) = 8841.$

H	K	L	$\|F\|_{OBS}$	$\|F\|_{CALC}$
2	0	0	6.9	8.8
4	0	0	150.4	137.9
6	0	0	11.9	11.2
8	0	0	7.2	4.8
10	0	0	292.3	297.1
12	0	0	146.4	137.5
14	0	0	13.8	11.4
16	0	0	238.5	236.4
18	0	0	46.9	48.9
20	0	0	112.1	109.0
22	0	0	11.5	15.7
24	0	0	94.1	94.8
26	0	0	77.0	75.7
28	0	0	87.5	90.5
30	0	0	8.4	8.9
2	2	0	2.9	3.5
4	2	0	49.6	54.7
6	2	0	24.1	24.4
8	2	0	37.8	42.4
10	2	0	61.4	56.6
12	2	0	10.9	13.8
14	2	0	2.9	4.1
16	2	0	38.6	40.7
18	2	0	18.1	18.9
20	2	0	51.4	52.0
22	2	0	4.2	4.0
24	2	0	13.1	12.6
26	2	0	62.5	62.0
28	2	0	24.3	19.7
4	4	0	26.5	23.8
6	4	0	85.8	84.3
8	4	0	46.6	43.0
10	4	0	132.6	132.5
12	4	0	76.0	73.1
14	4	0	56.3	59.4
16	4	0	46.3	44.7
18	4	0	6.3	5.4
20	4	0	56.2	56.9
22	4	0	10.5	5.5
24	4	0	25.8	25.0
26	4	0	51.9	50.5
28	4	0	5.1	8.2
6	6	0	100.3	97.0
8	6	0	71.2	70.6
10	6	0	148.0	148.6
12	6	0	55.5	54.5
14	6	0	32.4	35.6
16	6	0	24.7	25.4
18	6	0	7.5	3.7
20	6	0	94.1	95.6
22	6	0	44.6	44.5
24	6	0	37.0	37.8
26	6	0	28.0	29.3
28	6	0	18.0	16.3
8	8	0	77.4	78.7
10	8	0	56.1	52.6
12	8	0	64.2	67.8
14	8	0	88.6	89.6
16	8	0	25.9	24.6
18	8	0	3.6	3.6
20	8	0	17.1	13.9
22	8	0	10.5	8.4
24	8	0	20.3	11.9
26	8	0	40.0	41.3
28	8	0	4.7	3.8
10	10	0	87.6	84.7
12	10	0	75.3	68.9
14	10	0	21.2	17.7
16	10	0	131.2	134.9
18	10	0	56.4	51.7
20	10	0	101.1	100.2
22	10	0	48.4	49.9
24	10	0	66.1	64.5
26	10	0	33.5	26.7
28	10	0	3.6	2.7
12	12	0	14.7	10.7
14	12	0	34.4	31.3
16	12	0	55.1	52.1
18	12	0	38.3	40.3
20	12	0	50.7	47.8
22	12	0	34.9	31.0
24	12	0	5.1	4.9
26	12	0	5.5	6.3
14	14	0	20.8	21.9
16	14	0	69.6	71.1
18	14	0	7.5	4.0
20	14	0	50.3	48.1
22	14	0	51.3	49.2
24	14	0	28.7	24.8
26	14	0	69.8	67.5
16	16	0	69.2	69.7
18	16	0	36.9	37.8
20	16	0	99.4	101.9
22	16	0	27.7	24.6
24	16	0	40.2	42.7
18	18	0	83.9	80.1
20	18	0	24.0	23.3
22	18	0	5.5	3.6
24	18	0	25.2	24.0
20	20	0	56.4	58.2
22	20	0	44.8	50.5
5	3	1	78.5	77.5
7	3	1	5.5	2.8
9	3	1	75.7	75.2
11	3	1	8.6	9.0
13	3	1	29.5	29.9
15	3	1	6.6	4.3
17	3	1	95.8	97.8
19	3	1	36.6	37.6

H	K	L	$\|F\|_{OBS}$	$\|F\|_{CALC}$
21	3	1	11.1	13.5
23	3	1	18.8	18.2
25	3	1	22.7	23.4
27	3	1	46.9	44.0
29	3	1	5.7	5.7
7	5	1	37.4	29.5
9	5	1	52.5	49.3
11	5	1	3.6	0.8
13	5	1	29.2	25.6
15	5	1	41.8	41.8
17	5	1	25.7	26.9
19	5	1	7.2	4.5
21	5	1	2.9	1.1
23	5	1	2.9	1.8
25	5	1	15.1	16.1
27	5	1	10.3	12.2
29	5	1	34.9	34.2
9	7	1	3.6	2.9
11	7	1	21.2	14.9
13	7	1	23.4	20.5
15	7	1	7.8	7.2
17	7	1	18.6	15.6
19	7	1	5.5	3.4
21	7	1	12.2	8.3
23	7	1	8.4	9.1
25	7	1	21.6	21.2
27	7	1	9.6	9.7
29	7	1	7.5	5.7
11	9	1	19.9	20.1
13	9	1	59.4	58.8
15	9	1	40.8	41.8
17	9	1	21.0	22.2
19	9	1	9.4	7.2
21	9	1	6.3	1.3
23	9	1	24.2	25.2
25	9	1	40.8	35.6
27	9	1	28.7	28.4
13	11	1	62.6	64.3
15	11	1	20.7	25.7
17	11	1	18.1	21.5
19	11	1	6.3	3.7
21	11	1	16.7	15.9
23	11	1	5.9	2.0
25	11	1	27.3	27.4
27	11	1	11.3	8.7
15	13	1	25.4	24.2
17	13	1	8.4	6.3
19	13	1	10.1	6.9
21	13	1	18.7	17.2
23	13	1	15.7	13.3
25	13	1	31.3	28.5
27	13	1	18.1	17.2
17	15	1	2.1	0.4
19	15	1	29.3	27.6
21	15	1	31.1	30.4
23	15	1	24.5	22.6
25	15	1	37.9	38.3
19	17	1	29.1	29.8
21	17	1	8.6	5.4
23	17	1	37.7	40.5
21	19	1	25.8	24.5
23	19	1	3.6	0.8
2	2	2	74.6	78.4
4	2	2	32.2	18.7
6	2	2	104.1	103.5
8	2	2	85.0	85.8
10	2	2	39.5	38.7
12	2	2	121.5	118.1
14	2	2	69.0	68.2
16	2	2	4.7	3.5
18	2	2	164.0	175.7
20	2	2	29.8	32.9
22	2	2	57.8	57.9
24	2	2	67.3	70.1
26	2	2	8.6	6.8
28	2	2	92.8	86.8
4	4	2	95.2	86.1
6	4	2	4.7	0.5
8	4	2	20.3	18.3
10	4	2	19.1	22.3
12	4	2	42.6	40.6
14	4	2	63.8	52.5
16	4	2	0.	5.2
18	4	2	41.9	38.3
20	4	2	3.6	1.1
22	4	2	19.7	15.3
24	4	2	22.2	20.3
26	4	2	11.1	8.6
28	4	2	52.6	50.8
6	6	2	49.1	43.5
8	6	2	137.5	136.1
10	6	2	41.1	39.5
12	6	2	73.4	72.0
14	6	2	14.2	16.3
16	6	2	37.9	41.8
18	6	2	26.9	25.3
20	6	2	11.3	13.7
22	6	2	13.9	10.5
24	6	2	30.6	29.9
26	6	2	26.0	25.4
28	6	2	15.4	14.9
8	8	2	162.2	153.5
10	8	2	31.8	32.7
12	8	2	65.0	65.7
14	8	2	32.9	27.4
16	8	2	64.8	63.6
18	8	2	143.8	147.3
20	8	2	20.2	19.3
22	8	2	61.7	62.8

H	K	L	$\|F\|_{OBS}$	$\|F\|_{CALC}$
24	8	2	61.7	58.5
26	8	2	27.2	27.2
28	8	2	60.1	60.4
10	10	2	34.1	30.5
12	10	2	2.1	1.5
14	10	2	25.8	25.2
16	10	2	35.9	34.1
18	10	2	32.7	32.3
20	10	2	30.6	30.7
22	10	2	11.7	12.4
24	10	2	10.5	9.1
26	10	2	32.6	30.4
28	10	2	11.1	7.2
12	12	2	103.9	107.0
14	12	2	71.4	70.9
16	12	2	14.2	12.1
18	12	2	63.8	65.7
20	12	2	11.3	9.6
22	12	2	72.0	72.0
24	12	2	48.9	46.2
26	12	2	3.6	1.3
14	14	2	26.1	20.4
16	14	2	2.9	1.4
18	14	2	55.7	57.5
20	14	2	18.6	21.7
22	14	2	12.2	8.6
24	14	2	13.1	10.4
26	14	2	16.3	14.4
16	16	2	26.6	33.1
18	16	2	17.6	15.2
20	16	2	5.1	7.8
22	16	2	6.3	4.1
24	16	2	28.8	28.0
18	18	2	79.1	74.3
20	18	2	30.9	31.4
22	18	2	54.6	51.7
24	18	2	16.3	20.4
20	20	2	21.3	15.9
22	20	2	14.1	12.8
7	5	3	76.0	74.3
9	5	3	2.9	4.2
11	5	3	17.7	16.0
13	5	3	23.1	22.0
15	5	3	45.8	47.6
17	5	3	2.9	3.1
19	5	3	4.2	1.5
21	5	3	15.4	14.7
23	5	3	32.8	33.3
25	5	3	9.6	2.2
27	5	3	19.7	16.1
29	5	3	26.1	24.9
9	7	3	2.9	0.5
11	7	3	33.8	31.9
13	7	3	5.5	8.4
15	7	3	25.1	21.8
17	7	3	43.6	42.8
19	7	3	18.2	16.7
21	7	3	6.3	8.1
23	7	3	18.8	12.5
25	7	3	15.0	14.1
27	7	3	21.1	17.4
29	7	3	6.9	9.5
11	9	3	16.0	13.8
13	9	3	25.8	29.8
15	9	3	50.9	52.7
17	9	3	29.8	34.8
19	9	3	8.1	0.8
21	9	3	5.1	3.0
23	9	3	16.5	12.4
25	9	3	8.6	6.3
27	9	3	5.5	6.7
13	11	3	71.5	75.5
15	11	3	28.9	32.0
17	11	3	29.0	28.3
19	11	3	4.2	4.7
21	11	3	5.9	1.5
23	11	3	30.1	33.0
25	11	3	5.9	1.0
27	11	3	4.2	1.5
15	13	3	6.6	5.0
17	13	3	11.7	11.4
19	13	3	4.7	0.4
21	13	3	3.6	1.5
23	13	3	31.9	33.4
25	13	3	5.9	5.6
17	15	3	10.5	8.7
19	15	3	5.5	2.9
21	15	3	21.0	19.0
23	15	3	6.6	2.8
25	15	3	40.9	39.6
19	17	3	29.8	29.3
21	17	3	14.7	12.2
23	17	3	9.6	5.9
21	19	3	17.5	15.2
23	19	3	2.9	2.9
4	4	4	60.8	62.1
6	4	4	54.8	55.0
8	4	4	108.7	101.4
10	4	4	95.0	97.6
12	4	4	13.3	7.8
14	4	4	16.0	16.8
16	4	4	7.2	5.9
18	4	4	14.6	13.9
20	4	4	70.1	70.3
22	4	4	7.2	6.9
24	4	4	12.2	14.2
26	4	4	33.7	30.5
28	4	4	13.1	17.0
6	6	4	144.3	145.1

H	K	L	$\|F\|_{OBS}$	$\|F\|_{CALC}$
8	6	4	4.7	6.3
10	6	4	119.5	121.2
12	6	4	22.1	19.4
14	6	4	36.8	40.7
16	6	4	19.4	16.4
18	6	4	8.4	8.9
20	6	4	37.7	36.9
22	6	4	16.4	19.5
24	6	4	5.1	1.9
26	6	4	23.5	22.8
28	6	4	4.2	7.8
8	8	4	92.2	92.3
10	8	4	12.1	14.3
12	8	4	14.1	13.5
14	8	4	109.6	113.2
16	8	4	36.9	39.6
18	8	4	50.5	51.8
20	8	4	8.4	8.9
22	8	4	4.2	3.4
24	8	4	80.0	78.6
26	8	4	30.6	27.0
28	8	4	53.6	56.1
10	10	4	84.0	86.7
12	10	4	68.1	68.6
14	10	4	39.9	42.7
16	10	4	96.6	102.0
18	10	4	7.5	3.8
20	10	4	62.3	60.9
22	10	4	31.8	32.2
24	10	4	22.9	24.3
26	10	4	52.6	55.8
28	10	4	9.4	11.1
12	12	4	107.4	107.2
14	12	4	11.7	15.3
16	12	4	18.8	18.8
18	12	4	40.9	42.6
20	12	4	19.8	15.6
22	12	4	44.5	43.1
24	12	4	25.9	27.4
26	12	4	10.1	8.8
14	14	4	4.7	7.8
16	14	4	19.9	21.9
18	14	4	4.7	3.9
20	14	4	23.9	18.3
22	14	4	5.9	0.6
24	14	4	6.9	0.8
26	14	4	23.4	20.6
16	16	4	25.1	25.6
18	16	4	12.9	16.1
20	16	4	48.0	44.0
22	16	4	10.3	5.8
24	16	4	5.5	3.3
18	18	4	43.7	45.3
20	18	4	0.	1.4
22	18	4	5.9	5.5
20	20	4	89.6	82.6
22	20	4	27.5	25.1
9	7	5	5.1	5.3
11	7	5	36.1	34.5
13	7	5	51.9	52.9
15	7	5	71.2	72.7
17	7	5	18.2	19.6
19	7	5	7.5	10.8
21	7	5	5.9	3.7
23	7	5	30.5	26.3
25	7	5	35.8	32.6
27	7	5	10.1	5.1
11	9	5	16.7	14.2
13	9	5	78.9	79.6
15	9	5	18.2	17.6
17	9	5	2.9	5.1
19	9	5	6.3	0.4
21	9	5	4.7	1.4
23	9	5	12.9	10.9
25	9	5	30.2	29.5
27	9	5	19.3	18.3
13	11	5	6.3	7.4
15	11	5	24.2	26.2
17	11	5	19.3	18.0
19	11	5	24.0	26.7
21	11	5	17.2	16.8
23	11	5	9.8	8.6
25	11	5	4.2	3.6
27	11	5	12.6	11.6
15	13	5	11.5	11.8
17	13	5	12.4	13.0
19	13	5	4.2	2.3
21	13	5	27.4	26.7
23	13	5	6.3	4.3
25	13	5	30.2	29.2
17	15	5	30.2	30.2
19	15	5	10.3	9.5
21	15	5	16.8	17.7
23	15	5	2.9	1.4
25	15	5	9.1	8.0
19	17	5	39.7	40.0
21	17	5	2.1	1.1
23	17	5	27.5	23.7
21	19	5	23.0	24.6
6	6	6	22.5	19.6
8	6	6	12.8	16.0
10	6	6	132.9	127.3
12	6	6	35.6	34.6
14	6	6	112.6	119.7
16	6	6	42.0	43.6
18	6	6	28.2	25.7
20	6	6	63.4	64.8
22	6	6	17.7	15.3
24	6	6	43.1	41.5

Table 3 (cont.)

H	K	L	$|F|_{OBS}$	$|F|_{CALC}$	H	K	L	$|F|_{OBS}$	$|F|_{CALC}$	H	K	L	$|F|_{OBS}$	$|F|_{CALC}$	H	K	L	$|F|_{OBS}$	$|F|_{CALC}$
26	6	6	58.4	56.3	15	11	7	11.5	9.7	16	16	8	12.6	12.7	20	16	10	89.2	85.5
28	6	6	4.7	2.9	17	11	7	25.5	24.5	18	16	8	37.3	35.5	22	16	10	23.3	23.7
8	8	6	72.5	67.3	19	11	7	16.4	16.2	20	16	8	3.6	5.8	18	18	10	49.2	48.8
10	8	6	19.4	15.5	21	11	7	27.7	26.4	22	16	8	5.5	3.4	20	18	10	18.6	18.2
12	8	6	68.9	67.1	23	11	7	14.2	8.8	24	16	8	8.6	10.1	20	20	10	67.2	67.6
14	8	6	31.0	28.2	25	11	7	15.7	16.3	18	18	8	99.1	96.6	15	13	11	6.3	6.1
16	8	6	53.1	58.6	27	11	7	4.7	2.3	20	18	8	31.3	32.2	17	13	11	22.7	21.7
18	8	6	57.5	60.6	15	13	7	5.1	5.2	22	18	8	69.0	67.3	19	13	11	21.0	20.6
20	8	6	0.	1.6	17	13	7	9.4	10.5	20	20	8	38.6	34.2	21	13	11	29.6	27.3
22	8	6	39.5	39.1	19	13	7	21.7	20.6	13	11	9	10.9	13.1	23	13	11	13.1	13.6
24	8	6	21.1	21.2	21	13	7	53.7	54.3	15	11	9	10.9	9.1	17	15	11	22.4	22.0
26	8	6	2.9	1.0	23	13	7	37.9	40.6	17	11	9	12.4	10.6	19	15	11	26.5	23.7
28	8	6	10.5	9.7	25	13	7	57.4	52.2	19	11	9	16.5	18.3	21	15	11	51.2	49.2
10	10	6	104.2	100.2	17	15	7	4.7	2.6	21	11	9	29.8	31.5	23	15	11	6.6	6.2
12	10	6	57.5	55.9	19	15	7	5.5	4.9	23	11	9	27.0	21.6	19	17	11	22.6	24.0
14	10	6	49.1	55.2	21	15	7	42.0	40.3	25	11	9	4.7	3.9	21	17	11	4.7	6.6
16	10	6	86.7	84.7	23	15	7	2.1	2.1	15	13	9	4.7	0.6	12	12	12	93.1	95.8
18	10	6	6.3	1.6	25	15	7	6.9	1.4	17	13	9	18.0	18.6	14	12	12	27.4	31.1
20	10	6	42.6	40.5	19	17	7	8.4	5.3	19	13	9	18.3	20.7	16	12	12	10.3	8.2
22	10	6	19.8	21.0	21	17	7	48.1	44.5	21	13	9	56.4	53.7	18	12	12	37.8	38.2
24	10	6	30.8	31.0	23	17	7	6.3	3.2	23	13	9	25.1	27.9	20	12	12	7.5	3.3
26	10	6	56.4	61.0	21	19	7	19.9	20.0	25	13	9	11.1	7.1	22	12	12	15.9	15.9
12	12	6	57.0	56.9	8	8	8	37.2	38.9	17	15	9	11.5	12.3	24	12	12	28.4	30.6
14	12	6	6.3	0.6	10	8	8	14.7	15.1	19	15	9	28.0	25.8	14	14	12	21.6	22.0
16	12	6	19.8	21.5	12	8	8	41.7	42.7	21	15	9	4.2	2.2	16	14	12	4.7	0.5
18	12	6	27.1	27.2	14	8	8	163.9	169.7	23	15	9	45.2	42.8	18	14	12	72.7	71.6
20	12	6	16.8	13.6	16	8	8	95.4	96.3	19	17	9	8.1	8.3	20	14	12	19.6	20.7
22	12	6	21.6	23.1	18	8	8	95.3	97.5	21	17	9	11.9	13.1	22	14	12	53.2	56.2
24	12	6	5.5	6.4	20	8	8	4.7	4.2	23	17	9	13.1	10.5	16	16	12	8.6	6.9
26	12	6	18.2	20.9	22	8	8	57.2	60.4	21	19	9	2.9	1.9	18	16	12	12.2	7.1
14	14	6	8.1	11.9	24	8	8	69.6	68.8	10	10	10	12.9	13.6	20	16	12	8.9	10.5
16	14	6	43.6	46.2	26	8	8	44.0	45.1	12	10	10	55.9	52.4	22	16	12	13.9	14.2
18	14	6	8.1	6.0	10	10	8	49.7	47.9	14	10	10	60.4	60.4	18	18	12	55.3	52.8
20	14	6	8.1	5.4	12	10	8	66.7	67.4	16	10	10	106.2	106.9	20	18	12	4.2	2.0
22	14	6	7.5	8.4	14	10	8	37.4	41.3	18	10	10	31.1	37.2	17	15	13	15.1	12.6
24	14	6	20.7	23.3	16	10	8	10.7	15.1	20	10	10	59.3	53.0	19	15	13	4.7	6.5
16	16	6	36.2	34.6	18	10	8	12.1	14.7	22	10	10	44.5	44.0	21	15	13	6.6	4.4
18	16	6	24.5	25.8	20	10	8	40.8	38.9	24	10	10	113.3	111.0	19	17	13	24.2	23.4
20	16	6	64.0	63.1	22	10	8	49.5	47.8	26	10	10	29.3	32.6	21	17	13	6.3	7.4
22	16	6	50.0	49.0	24	10	8	8.6	6.1	12	12	10	27.8	20.7	14	14	14	9.4	12.2
24	16	6	3.6	2.4	26	10	8	21.2	23.6	14	12	10	9.4	9.0	16	14	14	2.9	3.0
18	18	6	11.7	4.8	12	12	8	68.3	69.4	16	12	10	35.8	36.8	18	14	14	15.1	14.6
20	18	6	23.0	17.7	14	12	8	70.3	73.1	18	12	10	27.3	26.3	20	14	14	62.6	56.1
22	18	6	46.1	46.1	16	12	8	13.4	11.0	20	12	10	36.6	32.7	22	14	14	25.8	22.6
20	20	6	61.0	57.6	18	12	8	67.3	70.1	22	12	10	6.3	1.5	16	16	14	80.7	77.6
11	9	7	4.7	4.1	20	12	8	29.6	30.4	24	12	10	17.8	20.8	18	16	14	7.8	7.9
13	9	7	54.1	57.6	22	12	8	56.9	57.1	14	14	10	27.3	27.1	20	16	14	25.5	23.5
15	9	7	17.2	19.4	24	12	8	53.6	51.7	16	14	10	41.0	40.1	18	18	14	35.8	36.0
17	9	7	4.2	1.4	26	12	8	23.6	22.0	18	14	10	15.7	18.1	19	17	15	7.8	9.9
19	9	7	10.7	11.1	14	14	8	10.3	5.6	20	14	10	53.3	49.1	16	16	16	7.5	7.9
21	9	7	6.9	4.2	16	14	8	9.1	8.2	22	14	10	25.6	22.9	18	16	16	21.7	20.4
23	9	7	10.1	8.1	18	14	8	30.9	32.0	24	14	10	34.6	31.4	18	18	16	12.9	18.3
25	9	7	15.6	13.2	20	14	8	37.0	35.2	16	16	10	102.5	101.4					
27	9	7	4.7	5.1	22	14	8	9.1	6.9	18	16	10	12.6	14.3					
13	11	7	69.2	71.7	24	14	8	58.9	59.6										

pendicular to the mid-points of the external bonds lying along the fivefold axes. The resultant grouping shown in Fig. 2 is the basic unit in the framework of YB$_{66}$. Here the central icosahedron has been inscribed in a sphere; the outer icosahedra are represented by the spheres that circumscribe them. The centers of mass of the outer icosahedra form an icosahedron concentric with the central icosahedron. The 156 atom unit is thus composed of a central icosahedron surrounded icosahedrally by icosahedra. As a result of this geometry, the twelve outer icosahedra are bonded to one another by thirty bonds parallel to the edges of the large icosahedron formed by their centers of mass.

The configuration containing the 13 icosahedra occurs in β-rhombohedral boron (Hughes et al., 1963) but not as a packing unit; the outer icosahedra are shared by two central icosahedra in β-rhombohedral boron and hence the packing unit there is the 84-atom group obtained by truncation of the outer icosahedra to leave only pentagonal pyramids surrounding the central icosahedron. Thus, the YB$_{66}$ structure contains icosahedral packing to a higher degree than the β-rhombohedral structure.

In YB$_{66}$ the thirteen-icosahedron unit is found in one orientation at the origin of the cell and by translation at the face centers. It also occurs at the centers

of the edges rotated by 90°. The large units are connected as shown in Fig. 3 which includes only the icosahedra centered in the xy0 plane. Each of the outer

Fig. 1. The icosahedron about the origin.

icosahedra of the 156 atom unit forms four bonds nearly along the pseudo fivefold axes of the icosahedra to similar members of neighboring units. These bonds are of two types. One group lies parallel to (100) faces and, along with the icosahedral edges, forms octagons around a fourfold axis. The second variety connects outer icosahedra in adjacent units along directions which do not lie in or parallel to (100) planes. These bonds are involved in hexagonal rings. Through such interunit bonding the framework perpetuates itself. Fig. 4 shows the 13-icosahedron units which intersect the $xy0$ plane to demonstrate the relative orientations of the icosahedra within a unit as well as the inter-icosahedral bonds within and between the various units.
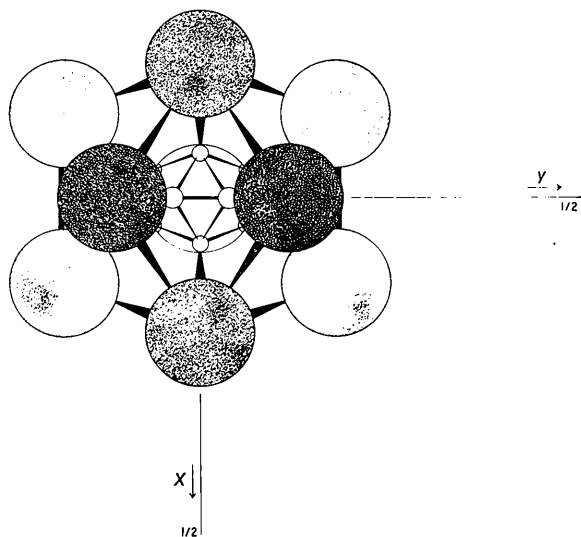
Fig. 2. The thirteen-icosahedron unit.
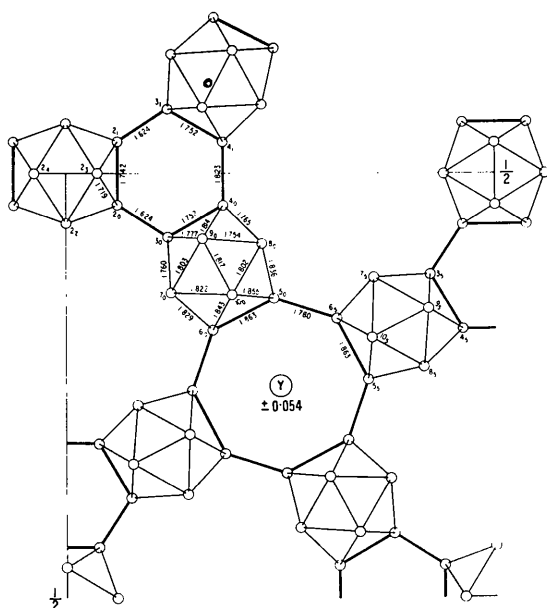
Fig. 3. Detailed bonding of the icosahedra in the $xy0$ plane.

Within the space occupied by the framework there exists a dense and efficient packing of icosahedra, at least as dense as in any of the forms of elemental boron. Since this packing is icosahedral it follows that it cannot fill all space and voids must of necessity occur. In YB_{66}, these voids are channels that run parallel to the fourfold axes at $\frac{1}{4}\frac{1}{4}x$. The yttrium atoms lie on the fourfold axes somewhat above or below the octagons of boron atoms at a point equidistant from the 4 triangular faces of the icosahedra bordering the octagon. The partially occupied yttrium positions occur in pairs, one above and one below the plane of the octagon. Either member of a pair may be occupied but it is unlikely that both are simultaneously occupied since the separation of the sites (1·955 Å) is too short for a pair of yttrium atoms.

Detailed bonding in the icosahedral framework

The icosahedra which make up the thirteen-icosahedron units and hence the framework are of two kinds. The central icosahedron of any given unit is quite regular. The two bond lengths,* given in Table 4, which define the edges of the figure, do not differ significantly from each other; the mean value is 1·726, $\sigma = 0 \cdot 006$ Å. The twelve outer icosahedra which surround this figure are somewhat larger and less regular than the central icosahedron. The mean bond length is 1·808 Å; the individual bonds show a trend toward lengthening as the distance from the central icosahedron increases (see Fig. 5). The independent bonds involved in these figures are listed in Table 4. The mean values of the edges for the two distinct icosahedra in YB_{66} and the presently available average edge lengths for the central and attached icosahedra in β-rhombohedral boron are compared below:

	YB_{66}	β-Rhombohedral boron
Central	1·726 Å	1·75 Å
Outer	1·808 Å	1·83 Å

The icosahedra are joined by three kinds of external bonds: (1) bonds between the central icosahedron and the outer icosahedra, (2) bonds among the twelve outer icosahedra of one packing unit and (3) bonds between the outer icosahedra of adjacent thirteen-icosahedron units. Similar distances in β-rhombohedral boron range in length from 1·65–1·75 Å. Within the thirteen-icosahedron units in YB_{66}, there are 42 intericosahedral bonds (12 of the first kind, 30 of the second) distributed in the following way:

			σ
(12)	2_0–3_0	1·624 Å	0·008 Å
(24)	7_3–9_0	1·705 Å	0·005 Å
(6)	4_0–4_1	1·823 Å	0·011 Å

The twelve bonds, of the type 2_0–3_0, are radial bonds between the central icosahedron and the twelve outer

---

* Bond lengths were computed using the *ORFFE* function-error program of Busing & Levy (1959b).

icosahedra. They are substantially shorter than any of the internal bonds and of a length appropriate to a single electron pair bond. The external bonds between the twelve outer icosahedra are longer than the radial bonds and fall into two categories. The six bonds which connect icosahedra in directions parallel to the cell axes are longer than the twenty-four which are at an angle to these directions. The bonds do not lie exactly along fivefold axes and hence do not form equal angles with the bonds in the icosahedra they connect. The third kind of external bond is found between 156-atom units. Each of the outer icosahedra of these units forms four bonds to a similar member of a neighboring 156-atom unit. These bonds may be divided into two classes: (1) 8_0–8_{19} of length 1·708 Å, $\sigma = 0·008$ Å, which are involved in hexagonal rings and (2) 5_0–6_5 of length 1·780 Å, $\sigma = 0·008$ Å, forming the edges of an octagon. The two remaining boron atoms on each outer icosahedron are not involved in external bonds to other similar figures. Fig. 3 shows the icosahedra which intersect the $xy0$ plane and their connections. Here the independent atoms and some of their symmetrical equivalents are labelled. Where possible the intraicosahedral and intericosahedral bond lengths are included. In general, the intericosahedral bonds lie essentially along the pseudo fivefold axes of the icosahedra they connect. In a regular icosahedron the angle between a fivefold axis and the five adjacent edges is 121°43′; the comparable angles formed by each of the five kinds of external bond with the icosahedra in YB$_{66}$ are not all equal but exhibit typical variations of from 0–5°. (This variation may be as much as 15° for bonds between 156-atom units.)

The environment of the yttrium, as mentioned previously, consists of a belt of four triangular faces from the icosahedra which surround it. The twelve atoms in these faces form bonds to the yttrium of the following lengths:

			σ
(4)	Y–5_0	2·710 Å	0·005 Å
(4)	Y–6_0	2·691 Å	0·005 Å
(4)	Y–10_0	2·768 Å	0·004 Å

These distances may be compared to the yttrium–boron separation in YB$_{12}$, 2·783 ± 0·012 Å (Matkovich, Economy, Giese & Barrett, 1965). The yttrium coordination is completed by the cage configurations in the channels.

The varieties of boron–boron bonds described above are divided naturally by their dimensions and functions into well defined groups. They cannot as yet, however, be conveniently pigeonholed into well defined categories of bond type but it is possible to make a few general remarks. Each of the boron atoms in the framework forms six bonds to other boron atoms. The mean values of the bond lengths in the two types of icosahedra are very similar to those reported for the corresponding icosahedra in β-rhombohedral boron. The twelve radial bonds connecting the central icosahedron to the outer ones are of a length appro-

priate to a single electron pair bond. The remaining external bonds cover a range of values from 1·705–1·823 Å. The radial bonds join icosahedra approximately along a common fivefold axis. All the other external bonds are at a small angle to the fivefold axes of the icosahedra they join.

Some clarification of the reasons for the observed differences in size of the two types of icosahedra, the variation in the intericosahedral distances, and the orientation of the intericosahedral bonds within the thirteen-icosahedron units can be brought about by
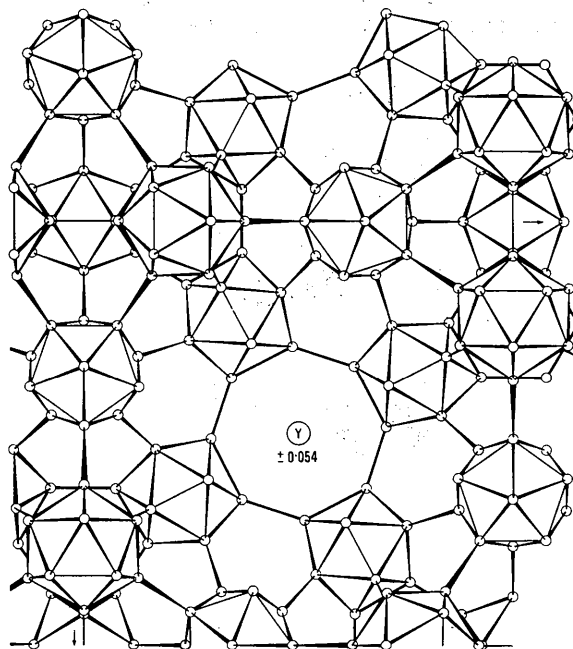
Fig. 4. The arrangement of the thirteen-icosahedron units in the $xy0$ plane.
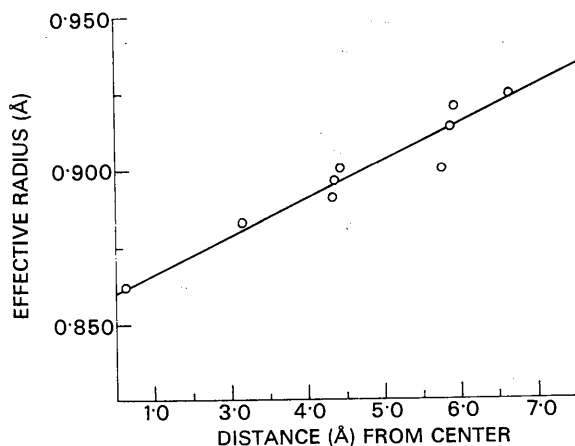
Fig. 5. The effective radius of a boron atom as a function of distance from the center of the thirteen-icosahedron unit. The radius is obtained from averaging the intraicosahedral bonds for each boron atom in the icosahedral framework.

considering the geometry of a similar unit made up of regular icosahedra.

Comments on the geometry of the 13-*icosahedron unit of boron atoms and its implications*

An array of twelve icosahedra whose centers of mass form an icosahedron around a central icosahedron can be generated from the central icosahedron by reflecting it through planes perpendicular to each of its twelve fivefold axes. The resulting icosahedra can be translated along the fivefold axes to achieve any desired radial intericosahedral separation. A slice through the unit including the centers of mass of the central icosahedron and two outer icosahedra is shown in Fig. 6.

From the geometry of the Figure, the following statements can be made.

(1) When constructed from equal regular icosahedra ($y = x$), the thirty bonds 'e' between outer icosahedra in this unit must always be longer than the twelve radial bonds 'r' between the central icosahedron and the outer shell. This is immediately obvious from the Figure since:

$$(2x + e) > E > 0 \cdot 951E \quad \text{and} \quad 0 \cdot 951E = 2x + r .$$

(2) When constructed of regular icosahedra of any size, the bonds 'e' in this unit can never lie along the fivefold axes of the outer icosahedra they connect, but rather make an angle of $5° 9'$ with each such axis.

Table 4. *Bond lengths in the boron framework**

Bond lengths in central icosahedron

			σ
(6)	$2_0 - 2_1$	1·742 Å	0·011 Å
(24)	$2_0 - 2_3$	1·719	0·007

Bond lengths in outer icosahedra

(1)	$3_0 - 4_0$	1·752 Å	0·008 Å	(2)	$6_0 - 10_0$	1·843 Å	0·005 Å
(2)	$3_0 - 7_0$	1·760	0·006	(1)	$7_0 - 7_{18}$	1·802	0·008
(2)	$3_0 - 9_0$	1·777	0·005	(2)	$7_0 - 9_0$	1·803	0·005
(2)	$4_0 - 8_0$	1·765	0·006	(2)	$7_0 - 10_0$	1·822	0·006
(2)	$4_0 - 9_0$	1·814	0·005	(1)	$8_0 - 8_{18}$	1·838	0·009
(1)	$5_0 - 6_0$	1·863	0·008	(2)	$8_0 - 9_0$	1·754	0·005
(2)	$5_0 - 8_0$	1·836	0·006	(2)	$8_0 - 10_0$	1·802	0·006
(2)	$5_0 - 10_0$	1·855	0·006	(2)	$9_0 - 10_0$	1·817	0·006
(2)	$6_0 - 7_0$	1·829	0·006				

Intericosahedral bonds

		σ
$2_0 - 3_0$	1·624 Å	0·008 Å
$7_3 - 9_0$	1·705	0·005
$8_0 - 8_{19}$	1·708	0·008
$5_0 - 6_5$	1·780	0·008
$4_0 - 4_1$	1·823	0·011

Yttrium–boron bonds

			σ
(4)	$Y - 5_0$	2·710 Å	0·005 Å
(4)	$Y - 6_0$	2·691	0·005
(4)	$Y - 10_0$	2·768	0·004

* Subscripts refer to the symmetry transformations:

Subscript	Transformed coordinates			Subscript	Transformed coordinates		
0	x	y	z	14	y	$\bar{x}$	$\frac{1}{2} - z$
1	$\bar{x}$	$\bar{y}$	z	15	$\bar{x}$	z	$\frac{1}{2} - y$
2	y	z	x	16	$\frac{1}{2} - z$	x	$\frac{1}{2} - y$
3	z	x	y	17	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$\frac{1}{2} - z$
4	z	$\bar{x}$	$\bar{y}$	18	$\bar{x}$	y	z
5	x	z	$\frac{1}{2} - y$	19	y	x	$\frac{1}{2} - z$
6	$\bar{x}$	y	$\bar{z}$	20	$\frac{1}{2} - z$	y	$\frac{1}{2} - x$
7	$\bar{z}$	x	$\bar{y}$	21	z	y	$\frac{1}{2} - x$
8	$\bar{z}$	$\bar{x}$	y	22	y	$\frac{1}{2} - x$	z
9	y	$\frac{1}{2} - z$	$\frac{1}{2} - x$	23	$\frac{1}{2} - z$	y	x
10	y	$\bar{z}$	$\bar{x}$	24	x	$\frac{1}{2} - z$	y
11	$\bar{y}$	z	$\bar{x}$	25	x	$\frac{1}{2} - y$	$\frac{1}{2} - z$
12	$\bar{y}$	$\bar{z}$	x	26	$\frac{1}{2} - z$	$\frac{1}{2} - x$	y
13	$\bar{y}$	x	$\frac{1}{2} - z$				

The angle formed between E and $0.951E$ is $(180° - \alpha)/2$ $= 58°17'$. The angle between $0.951E$ and a radius, x, for the outer icosahedra is $63°26'$. Therefore $\gamma = 63°26'$ $- 58°17' = 5°9'$. Since 'e' is parallel to E, the angle between 'e' and 'x' which lies along the fivefold axis is γ and is not a function of 'x'. (Alternatively expressed, the fivefold axes passing through the vertices being joined by any bond 'e' are not collinear, but instead make an angle of $169°42'$.)

(3) A general expression for the relation between 'e' and 'r' and the radii x and y of the outer and inner icosahedra respectively may be written down as follows:

Since
$$r = 0.951E - x - y$$
and
$$e = E - 2x \cos \gamma$$

$$r - 0.951e = (1.902 \cos \gamma - 1)x - y$$
$$= 0.894x - y .$$

In terms of the bond lengths defining the inner and outer icosahedra, B_I and B_O

$$r - 0.951e = 0.850B_O - 0.951B_I .$$

The relations between these quantities are of interest in two special cases:

(a) Equal icosahedra: $B_O = B_I$,

$$e = 1.052r + 0.106B_O .$$

(b) Equal intericosahedral bonds: $r = e$. (Consider allowing the outer icosahedra to expand or inner to contract to produce equal bonds.)

$$B_O = 0.058r + 1.12B_I ,$$
$$B_I = 0.894B_O - 0.052r .$$

In applying the above considerations to a unit constructed of boron atoms it is immediately apparent from (1) that such a unit cannot be constructed of equivalent regular icosahedra of boron atoms connected by single electron pair bonds (or equal bonds of any length) even if the requisite electrons were available. Further, from (2), although the orientation of the twelve radial connections 'r' is by construction along the common fivefold axes of the central and outer icosahedra, the orientation of the outer icosahedra is such that vertices of adjacent icosahedra do not share a common fivefold axis and the thirty connections 'e' are at a $5°9'$ angle to the fivefold axis passing through each of the vertices they connect.

It follows from 3(a) that if equal icosahedra, where $B_I = B_O = 1.81$ Å, are connected radially by single electron pair bonds, $r = 1.62$ Å, then $e = 1.89$ Å. The 1.89 Å distance is longer than any reported intericosahedral bond. Assuming, of course, regular icosahedra, the variables in the equation cannot be adjusted to appreciably reduce this value. (Taking an extreme situation where $r = 1.60$ Å and $B_O = 1.72$ Å, $e = 1.86$ Å.) The quantity 'e' is relatively independent of B_O and effec-

tively proportional to 'r'. Any increase in 'r' would serve to further increase 'e'; to decrease 'r' to less than 1.60 Å is physically unreasonable. Therefore, if this unit were to be constructed of equal regular icosahedra, the figure would have to contain thirty intericosahedral bonds 'e' of exceptional length.

If, on the other hand, the outer icosahedra are allowed to expand as expressed in 3(b) to produce equal single electron pair bonds, an unrealistic value of B_O will be obtained which is relatively insensitive to the value of 'r'. That is, the ratio of B_O to B_I is required to be too large under these conditions. For example, for $r = 1.62$ Å, $B_I = 1.81$ Å, $B_O = 2.12$ Å; or for $r = 1.62$ Å, $B_I = 1.75$ Å, $B_O = 2.05$ Å. Conversely, of course, reasonable values of B_O yield unreasonably small values of B_I.

Inequality in the size of the icosahedra and in the bonds connecting them is to be expected, therefore, for any actual structure with the thirteen-icosahedron unit, *solely on the basis of geometry*; in addition, fivefold symmetry cannot be maintained for all of the bonds connecting icosahedra. Energetic factors pertaining to bond formation may further emphasize these features and also cause the icosahedra to distort and become irregular. It is interesting to see how well

FOR REGULAR ICOSAHEDRA

$\alpha = 63° 26'$

$\beta = 121° 43'$

$\gamma = 5° 9'$
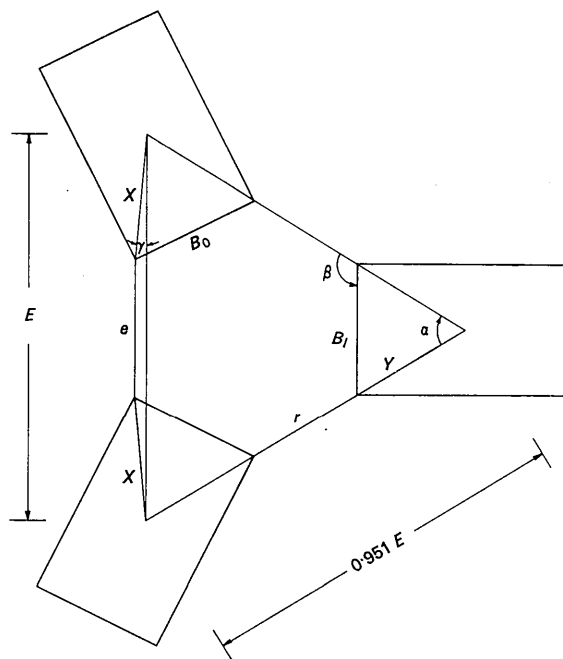
Fig. 6. A section through the thirteen-icosahedron unit including the centers of mass of the central icosahedron (to the right) and two outer icosahedra.

the actual thirteen-icosahedron units in crystal structures conform to the equations deduced here for regular icosahedra. In both β-rhombohedral boron and YB$_{66}$ the individual icosahedra are distorted; however, it is possible to substitute values for their mean bond lengths into the general expression for unequal icosahedra. Taking this expression from 3 we can define a residual, Δ, which would be zero for the idealized figure,

$$\Delta = -r + 0.951e + 0.850B_O - 0.951B_I .$$

Using the values reported by Hughes et al. (1963) for β-rhombohedral boron one finds for the two cases:

	β-Rhombohedral boron	YB$_{66}$
r	1.65 Å	1.624 Å
e	1.75 Å	1.732 Å
B_O	1.83 Å	1.808 Å
B_I	1.75 Å	1.726 Å
Δ	−0.09 Å	−0.08 Å

Thus, neither structure conforms exactly to the ideal geometry; instead both deviate to about the same extent.

It is evident that the thirteen-icosahedron arrangement found here cannot be conveniently augmented by adding to the periphery to form an even larger packing unit maintaining icosahedral packing. A second complete shell of 72 icosahedra might be accommodated around the first shell of 12 by sufficient distortion, but since each additional shell requires expansion of the icosahedra, these figures themselves would become unstable in the third shell.

Contents of the channels

The boron positions which describe the contents of the channels are characterized by two special features. First, these sites, even as the yttrium sites, are not fully occupied; secondly the thermal ellipsoids for these atoms are considerably larger than those of the filled icosahedral sites. From the mean atomic positions, one can deduce two cage-like configurations which exist in the channels above the yttrium around

the 8(a) special positions. In one configuration the atoms 11 and 12 fully occupy these positions; in the other, atoms 11, 12 and 13 occur at 50% occupancy.

The exact locations of atoms 11, 12 and probably 13 differ slightly depending on their environment. The bond distances listed are those calculated from the least-squares positions and should be interpreted as indicating only which bonds are likely to be long, in the nature of multi-center bonds, and which are short as in single electron pair bonds. The bond distances averaged over thermal motion assuming each atom to move independently will also be included for comparison. These represent maximum values of the bond lengths for these positions. One can achieve satisfactory bonding schemes in several ways by shifting the atomic positions within the confines of the thermal ellipsoids. In reality the disorder may be such that a variety of positions close to the mean positions may be assumed by both configurations, the precise values of the parameters varying in different regions of the crystal. Bond lengths derived by making reasonable shifts in the atomic coordinates of the order of 0.004 of the cell edge differ by 0.1–0.2 Å from those calculated using the mean positions. The root mean square components of thermal displacement along the principal axes are given in Table 5.

Configuration I

One of the cage-like arrangements above the yttrium is made up of atoms 11, 12 and 13 at 50% occupancy. A portion of the unit is shown in Fig. 7. This represents an arbitrary choice of orientation in that the same figure rotated by 90° is equally likely to occur when the positions not represented here are filled. The triangles whose bases form the heavily outlined octagon are the faces of the four icosahedra which surround the fourfold axis. The figures formed by atoms 11, 12 and 13 encompass the 8(a) special positions, e.g. $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, which lie at the intersections of three channels. Each cage is at the center of a large octahedron of yttrium sites. Facing each of the six potential yttrium positions is a six membered ring. The thirty six statistical atoms

Table 5. Root mean square component of thermal displacement along the principal axes of thermal motion: R_1, R_2, R_3

Atom number*	R_1	σ	R_2	σ	R_3	σ
1	0.115 Å	0.002 Å	0.115 Å	0.002 Å	0.120 Å	0.003 Å
2	0.095	0.013	0.102	0.012	0.118	0.012
3	0.092	0.014	0.119	0.012	0.121	0.011
4	0.087	0.015	0.109	0.012	0.116	0.012
5	0.086	0.016	0.097	0.012	0.100	0.012
6	0.091	0.014	0.105	0.012	0.112	0.011
7	0.086	0.012	0.111	0.009	0.142	0.007
8	0.084	0.010	0.105	0.009	0.139	0.007
9	0.086	0.010	0.107	0.009	0.139	0.007
10	0.089	0.010	0.121	0.008	0.146	0.007
11	0.093	0.020	0.212	0.011	0.233	0.015
12	0.198	0.017	0.235	0.017	0.330	0.016
13	0.076	0.052	0.092	0.045	0.231	0.032
14	0.144	0.034	0.144	0.034	0.260	0.041

* Atom one is an yttrium atom; atoms two through fourteen are boron.

in this area are distributed in six such rings whose centers form an octahedron inside the large octahedron described by the yttrium positions. If an yttrium position is filled, all six atoms in the adjacent ring can form bonds to it.

(2)	Y–11$_0$	2·81 Å
(2)	Y–12$_9$	2·74 Å
(2)	Y–13$_9$	2·49 Å

Atoms of the type 11 and 13 bond to the icosahedral borons in the group represented by atom 10. This group contains the icosahedral borons which do not form external bonds to neighboring icosahedra. The bond lengths of these connections are:

| (2) | 10$_0$–11$_0$ | 1·74 Å |
| (2) | 10$_5$–13$_9$ | 1·98 Å |

This configuration can be visualized in the following way: having chosen an orientation for one ring, the orientation of the other five rings may be derived from it by the action of the threefold axes in the [111] directions of the unit cell, that is, through the triangle of atoms 11$_0$, 11$_2$, 11$_3$, or 12$_0$, 12$_9$, 12$_{16}$. The rings thus disposed are able to bond to one another. The arrangement of these bonds can be seen by examining the surroundings of atoms 11$_0$, 12$_9$ and 13$_9$. (As the remaining atoms in this unit are symmetrically related to these, their bonding is identical.) Each atom in a ring forms, of course, two bonds to its neighbors in the ring. Atoms 13 form two additional bonds to a nearby ring. Atoms of the type 11 and 12 form three additional bonds, two to one adjacent ring and one to another. The independent bond lengths calculated from the mean positions and averaged over thermal motion are given below the Figure. The independent triangles of atoms formed between the rings whose vertices are not related by a threefold axis are identified as A, B and C.

The cage forms 24 bonds to icosahedral borons, four from each of the six membered rings. The twenty four bonds may also be thought of as forming eight groups of three bonds related by a threefold axis leading to three icosahedra related by the same threefold axis.

In Fig. 8, the unit is shown in relation to the icosahedral framework. No effort has been made to put in all the external bonds. Rather this Figure is intended to illustrate the dimensional and spacial relationships of the 36 atom unit to the icosahedral framework.

Configuration II

The second configuration (Fig. 9) which occupies the channels and the one most likely to be present near filled yttrium sites is made up of atoms 11 and 12. The twenty four atoms of type 12 around each of the 8(a) sites are arranged in six squares which form a distorted snub cube. The snub cube is a polyhedron with six square faces at the corners of an octahedron and 32 triangular faces which connect the squares. Each square face is centered over an yttrium site, the corners forming bonds of 2·74 Å to this position.

The twenty four atoms 11 are arranged in eight triangles on the outside of the snub cube. These triangles are perpendicular to the [111] directions and are staggered with respect to the eight triangles of the snub cube which are also perpendicular to the [111] directions. The atoms 11 act as a filler between the snub cube and the icosahedral borons. They bond to the snub cube in the following manner. Two adjacent staggered triangles of atoms 11 and 12 form a very distorted octahedron; two adjacent distorted octahedra are connected by two distorted tetrahedra which share an edge. These features are shown in Fig. 9 which contains half of the 48 atom unit. The atoms 12 which make up the snub cube have been darkened. A distorted octahedron can be observed composed of atoms 11$_3$, 12$_{23}$, 12$_{24}$, 11$_2$, 11$_0$, 12$_{19}$; a distorted tetrahedron is formed by 11$_0$, 12$_{19}$, 12$_9$, 12$_{23}$. The atoms 11 also join this figure to the icosahedra surrounding it. Each atom 11 forms a bond to an icosahedral boron of the set 10 just as in configuration I. The atoms 11 also form bonds to the yttrium as in configuration I. Here, since
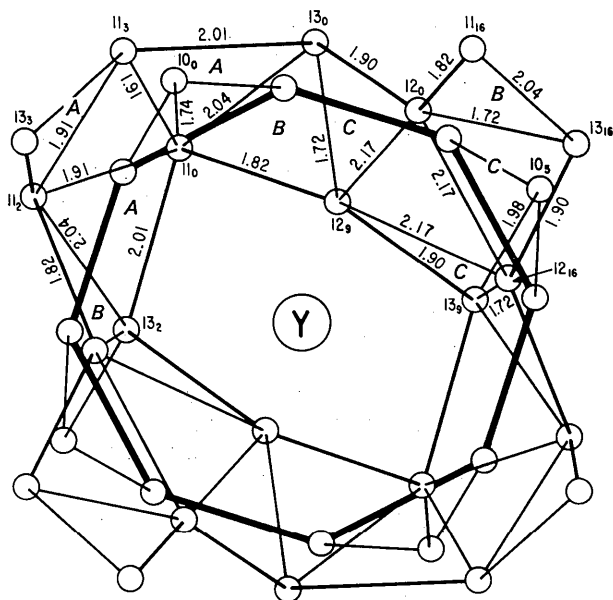
BOND LENGTHS AVERAGED OVER THERMAL MOTION

11$_0$–10$_0$	1.77Å
11$_0$–13$_2$	2.03Å
11$_0$–11$_2$	1.94 Å
11$_0$–13$_0$	2.07 Å
11$_0$–12$_9$	1.88Å
12$_9$–13$_0$	1.77Å
12$_9$–12$_0$	2.23Å
12$_9$–13$_9$	1.95Å
13$_9$–10$_5$	2.00Å

Fig. 7. Geometry and bond lengths of configuration I.

the sites are completely filled there are eight potential bonds (4 from atoms 11, 4 from atoms 12) to each yttrium position making a total maximum coordination number of 20 for the yttrium sites: 8 from configuration II, 12 from the icosahedral framework.

Both configuration I and configuration II as described are hollow cages. Atom 14 occurs in a set of 64 (g) *xxx etc.* positions which form a small cube around $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ at the center of the cage. These sites are only 1/4 occupied which could, for instance, correspond to filling a pair of sites separated by the body diagonal
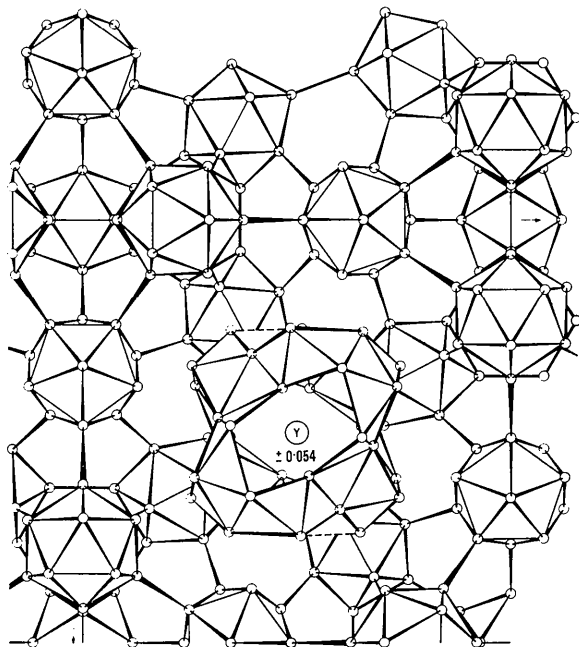
Fig. 8. Configuration I in relation to the icosahedral boron framework.
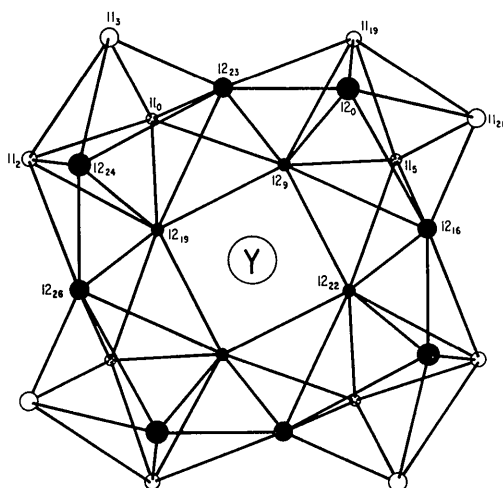
Fig. 9. A portion of the 48 atom unit: configuration II.

of the small cube. The calculated separation between these positions is 1·29 Å, $\sigma = 0.07$ Å, the same distance averaged over thermal motion is 1·32 Å, $\sigma = 0.07$ Å. These are much too short for boron–boron distances; but about right for an oxygen–oxygen separation. (Oxygen is a potential impurity in the structure.) One cannot however, discount the possibility that these atoms are boron. Because of their proximity to the special position $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ these coordinates are especially prone to error. In addition, the thermal ellipsoid is large and if boron and oxygen alternately fill the site, the calculated atomic position could be an average of these configurations. From the least-squares coordinates, atom 14 can form six bonds to atoms 12, three of length 1·95 Å, $\sigma = 0.03$ Å, three of length 2·08 Å, $\sigma = 0.02$ Å.

Fig. 10 displays the same atoms plotted in Fig. 9 with the addition of atom 14. The bond lengths, observed and averaged over thermal motion, are included beneath the Figure. The boron atoms forming the snub cube have a very high coordination number. For those interacting with an atom 14 the coordination number is 10, 9 bonds to boron atoms, 1 to yttrium. This high coordination is very unusual for boron, although nine coordination has been reported in β-rhombohedral boron. It is also somewhat illusory since some of the 'bonds' appear to be exceedingly long. The atoms 11 on the outside of the snub cube have coordination number six: five bonds to other boron atoms, one to yttrium.

The yttrium atom bonds to the twelve borons forming triangular faces of the icosahedra. Above the yttrium are the eight atoms which complete its coordination. In YB_6 and YB_{12} yttrium has a coordination number of twenty-four in contrast to twenty here. One might expect to find additional coordination achieved perhaps by a square of boron atoms around the neighboring yttrium site directly below the one shown. Unfortunately these positions lie about 1·3 Å from the yttrium position or very nearly in the positive ripple associated with a heavy atom represented by an incomplete Fourier series. This ripple is present in the observed Fourier, but at no point is its density quite as large as that of the least densely populated site discussed above. One can conclude then that there is no definite evidence for further coordination of the yttrium and if indeed such additional atoms exist in the crystal, the positions of the atoms are either buried in the heavy atom ripple or are quite random so as to smear out their contribution completely.

Fig. 11 is again a view of the thirteen-icosahedron units in the $xy0$ plane. This Figure is intended to show the spatial and dimensional relationships of the 48 atom unit, configuration II, to its surroundings. It is conceivable that additional configurations exist in which elements of the two configurations described above are combined. The exact conformation of any given cage may depend on the number and disposition of the filled yttrium sites around it.

Conclusions and summary

The YB$_{66}$ structure is a complex arrangement of icosahedra bonded to one another and to cage-like configurations of boron atoms trapped in channels of the icosahedral framework. The basic unit in the framework is a cluster of thirteen icosahedra, a central icosahedron surrounded icosahedrally by twelve icosahedra. This unit, characterized by a small central icosahedron surrounded by twelve larger ones, is also found in β-rhombohedral boron. The central icosahedron forms radial bonds along its pseudo fivefold axes to the twelve outer icosahedra. In turn these are joined

to one another by thirty longer bonds which are at an angle to the fivefold axes of the attached icosahedra. Although the individual bond lengths and angles vary widely and the icosahedra are distorted, the dimensional relationships observed within the thirteen-icosahedron unit as expressed by the mean bond lengths may be related to the geometry of a unit composed of regular icosahedra and seem to be a consequence of this geometry.

The coordination of the yttrium involves twelve boron atoms in four icosahedral faces and, at most, eight boron atoms from the cage-like configurations in the channels. In configuration II, the eight boron
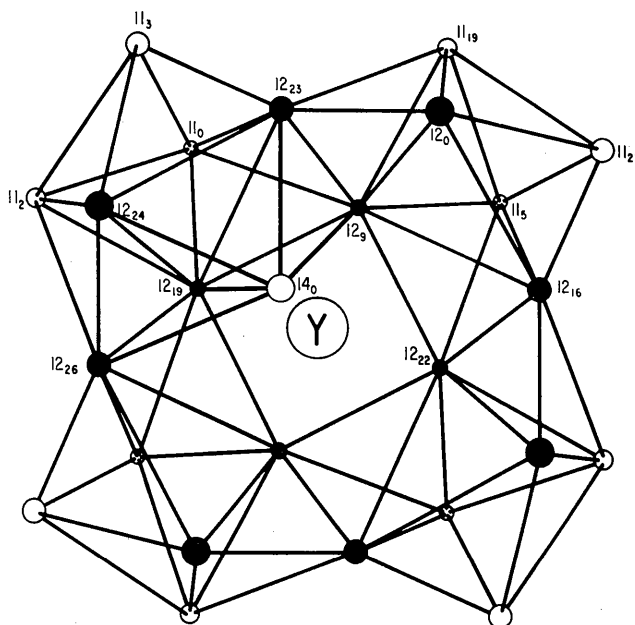
BOND LENGTHS	OBSERVED	AVERAGED OVER THERMAL MOTION
$11_0 - 10_0$	1.74 Å	1.77 Å
$11_0 - 11_2$	1.91 Å	1.94 Å
$11_0 - 11_3$	1.91 Å	1.94 Å
$11_0 - 12_9$	1.82 Å	1.88 Å
$11_0 - 12_{19}$	1.52 Å	1.60 Å
$11_0 - 12_{23}$	1.84 Å	1.89 Å
$12_9 - 11_0$	1.82 Å	1.88 Å
$12_9 - 11_5$	1.52 Å	1.60 Å
$12_9 - 11_{19}$	1.84 Å	1.89 Å
$12_9 - 12_0$	2.17 Å	2.23 Å
$12_9 - 12_{16}$	2.17 Å	2.23 Å
$12_9 - 12_{19}$	1.76 Å	1.83 Å
$12_9 - 12_{22}$	1.76 Å	1.83 Å
$12_9 - 12_{23}$	1.53 Å	1.62 Å
$12_9 - 14_0$	2.08 Å	2.14 Å
$12_{23} - 14_0$	1.95 Å	2.00 Å

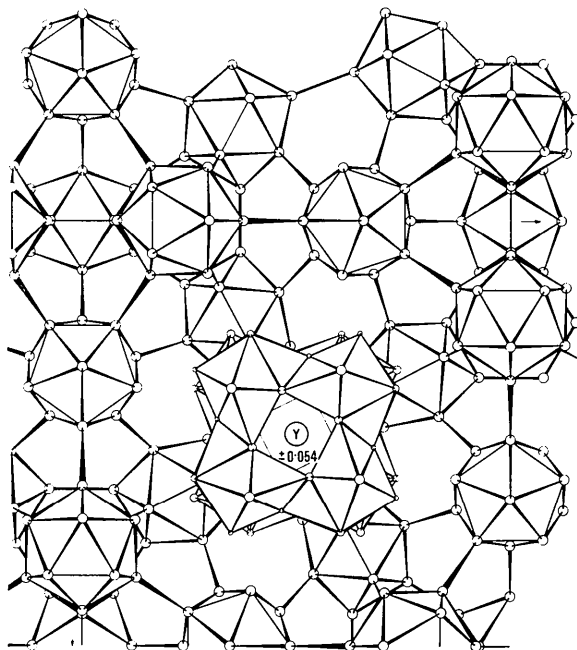Fig. 10. Configuration II: geometry and bond lengths.

Fig. 11. Configuration II in relation to the boron framework.

atoms are arranged in four triangles sharing corners. This mode of coordination to polyhedral faces is reminiscent of the clathrate structures and the cages which are found in YB_6 and YB_{12}. The function of the yttrium is probably as a donor of electrons to the boron framework in the manner of YB_6 and YB_{12}. Quite obviously the yttrium does not stabilize the icosahedra to the exclusion of other structural irregularities, but it does permit the existence of separate but interconnected thirteen-icosahedron units.

Although the novel arrangement of these icosahedra and their relationship to the yttrium sites in this structure is quite sharply defined, the configuration of the boron atoms around the intersections of the channels is not so readily apparent. One may construct from the observed atomic positions two possible configurations for this area; others may exist and in fact elements of each of the two described may combine to form a hybrid whose precise configuration would depend on

which of the surrounding yttrium sites were filled. There is ample opportunity for boron or foreign atoms to be trapped within these cages and there is some evidence that this is the case. It is also possible that by slow controlled crystallization the cage atoms could be induced to assume one unvarying arrangement. One might expect that the structures of the similar phases formed by Ho, Tb, Yb, Gd, and Pu will possess the same icosahedral boron frameworks, but it would be interesting to learn whether the contents of the channels remain the same. Additional analogous phases surely exist and further investigation into rare earth-boron systems should be worthwhile.

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