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Crystal Structure of $C_8Al_{2.1}B_{51}$

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X-ray analysis of $C_8Al_{2\cdot1}B_{51}$ ($C2/m\ 2/c\ 2_1/m$; $a=5\cdot690$, $b=8\cdot881$, $c=9\cdot100$ Å) based on full-matrix refinement of complete three-dimensional data gives a distorted hexagonal close-packed B_{12} icosahedral structure in which each icosahedral B atom is six coordinated. Half of the icosahedral B atoms form single B–B bonds between icosahedra; the remaining half are linked to C by single B–C bonds. Statistically distributed intericosahedral B atoms on a center of symmetry complete a tetrahedral environment about C and develop linear C–B–C chains similar to those found in rhombohedral boron carbide. Indeed, all B–B and B–C bond distances closely approximate values obtained for rhombohedral boron carbide. Aluminum atoms are located on partially occupied sites between icosahedra and in all cases Al–B and Al–C nearest neighbor contacts are at least 0·2 Å smaller than the sum of the appropriate covalent radii. Interestingly, an Al atom competes statistically with the B atom in the C–B–C chain such that when Al is present, B is not. The stoichiometry presented here leads to questions concerning the bonding schemes described in previous analyses based on different stoichiometries. Isotropic refinement gave $R_F=0\cdot050$ for 762 observed diffraction maxima.

Introduction

Crystal structures of compounds with high boron content have been of continual interest because boron carbide, the polymorphs of elemental boron and the compound considered here all contain B_{12} icosahedra, which, in conjunction with intericosahedral atoms, give interesting valence structures. Of the higher aluminum borides, only the structure of AlB_{10} has been reported (Will, 1963, 1966, 1967), and in this case there has been uncertainty regarding the stoichiometry and the nature of the intericosahedral atoms, in particular concerning the possible presence of carbon. The first point, stimulated by the non-integral number of 5·2 AlB_{10} molecules per unit cell, was considered (Lipscomb & Britton, 1960) in an illuminating discussion of the valence structures of the higher borides. One report (Matkovich, Economy & Giese, 1964) states that the true stoichiometry of AlB_{10} is C_4AlB_{24}, $Z=2$, and that carbon, necessary for crystal formation, links two icosahedra to form infinite chains. Additional results for C_4AlB_{24} were then submitted (Will, 1968) which suggested that C atoms joined three icosahedra and formed C–Al–C chains. Recently, in an excellent review article (Hoard & Hughes, 1967), it was suggested that the 'ternary compound of ideal formula for Al, B and C is C_4AlB_{26}, $Z=2$, and that carbon is present in C–B–C chains analogous to those in the structure of rhombohedral boron carbide. All Al atoms were assumed to be interstitial. From independent X-ray data collected on the same crystal used in the analysis based on AlB_{10}, which we now conclude to have the formula $C_8Al_{2\cdot1}B_{51}$ (per unit cell), we report the detailed structure of this interesting boride.

Structure determination

The space group, cell dimensions and density previously determined at this laboratory (Kohn, Katz & Giardini, 1958) are: $C2/m\ 2/c\ 2_1/m$; $a=5\cdot690\pm0\cdot001$, $b=8\cdot881\pm0\cdot001$, $c=9\cdot100\pm0\cdot002$ Å; $\varrho=2\cdot537\pm0\cdot003$ g.cm^{-3}. A total of 762 observed reflections were collected for *Hkl*, $0\leq H\leq11$ with Mo $K\alpha$ radiation and a moving crystal, moving counter technique with a G.E. XRD-6 semi-automatic diffractometer. In addition, 471 reflections with $\sin\theta/\lambda\leq1\cdot21$ were too small to be observed. Intensity data were corrected for Lorentz and polarization effects and converted to a set of structure factors. The tabular crystal had dimensions $0\cdot57\times0\cdot49\times0\cdot23$ mm; absorption corrections were not made. Unit weights were used for all refinements; however, the sensitivity of the final atomic parameters to the choice of weighting scheme was tested by refinement with weights inversely proportional to $|F|$. Although R_F increased slightly, the two methods showed no coordinate differences greater than 1·5 times the standard error of the determination (Table 1), and all but two were within the error.

A structure factor calculation based on coordinates given previously (Matkovich, Economy & Giese, 1964) yielded $R_F=0\cdot35$ for the five unique icosahedral *B* atoms. An initial three-dimensional Fourier synthesis was calculated by the use of 180 large structure factors, none of which changed sign during the remaining stages of the analysis. In addition to the B atoms of the icosahedra, four other maxima were located, one approximately as large as a B atom, the remaining three between one-sixth and one-third of a B atom in height.

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Utilizing only the B scattering curve, two cycles of least-squares refinement of the icosahedral atoms (1–5), the larger intericosahedral maximum (6) and one well-defined smaller maximum (9), followed by isotropic refinement of all temperature factors except that for atom 9 since full occupancy there was not expected lowered the discrepancy index to 0·15. The temperature factors of the icosahedral atoms were self-consistent and ranged from 0·45 to 0·52 Å², while that for atom 6 was 0·18. The remaining two maxima, in chemically unreasonable positions, were not tested; instead, a second three-dimensional electron density map was calculated yielding three additional small maxima. The first of these, atom 8, was added (with an adjusted multiplicity corresponding to its peak height); two cycles of refinement reduced R_F to 0·114. A second maximum further reduced R_F to 0·084. The last maximum from the Fourier synthesis was added but did not refine; it was not found in the final electron density map calculated from all observed structure factors. Finally, the atom multipliers of atoms 7–9 were refined. This, followed by coordinate and temperature refinement, gave $R_F=0{\cdot}067$ for a 9 atom all-boron structure.

In an attempt to determine the atomic numbers of intericosahedral atoms, bond distances were calculated. Intraicosahedral B–B linkages varied from 1·77 to 1·85 Å in agreement with expectations; atom 6 was linked to three icosahedral B atoms at 1·62 Å, a value very close to the sum of the covalent radii of B and C (0·9 and 0·77 Å, respectively). This, coupled with the low temperature factor of atom 6 and a careful electron microprobe analysis of the diffraction crystal itself which gave a C concentration at about the level of the boron carbide standard, allowed assignment of C to this position. Approximately 10·3 wt.% Al was also determined by microprobe analysis, but since C analysis is difficult by this method owing to hydrocarbon cracking and since no B analysis could be performed, the number of Al atoms could not be fixed with certainty. However, it appeared to be much closer to that required for C_4AlB_{24}, $Z=2$ than that for AlB_{10}, $Z=5{\cdot}2$.

The atomic arrangement about atom 9 shown in Fig. 1 was interpreted as follows. Atom 9 is on a center of symmetry fixing its coordinates. The carbon-atom 9 distance of 1·46 Å eliminates Al at that site leaving only C and B as possibilities. The extremely short 7–9 and non-centrosymmetrically related 7–7 distances of 1·20 and 1 23 Å respectively, eliminate both the simultaneous occupancy of sites 7 and 9 and uniform occupancy of site 7. Thus we concluded that when site 9 was occupied, 7 must be vacant, and that when 9 was vacant, at most a centrosymmetrically related pair of atoms was present at site 7. Other possibilities to include large thermal vibrations about the center of symmetry which could encompass site 7 or the presence of a single statistically distributed atom between 7 and 9 were not excluded. The latter possibility was eliminated on the basis of a structure factor calculation with a single atom replacing 7 and 9; this atom refined back to the center of symmetry. Large anisotropic thermal vibrations of atom 9 were subsequently excluded on the basis of anisotropic temperature factor calculations. The 6–7 distance of 1·77 Å is smaller than the sum of the covalent radii of Al(1·4 Å) and C, but greater than the sum of C and B so that no conclusions about atom 7 could be drawn on that basis. Atom 8, with nearest neighbor distances ranging from 1·95 to 2·01 Å, was considered to be aluminum.

At this point, the atoms occupying sites 9 and 7 were still in doubt and a test of the C_4AlB_{24} structure helped the atomic assignments. Atoms 1–5 were again assigned as B (fully occupied B icosahedra giving the required 48 B atoms), atom 6 was considered to be C giving the required 8 C atoms; this left three partially occupied intericosahedral sites which had to be aluminum. Complete refinement of all parameters gave $R_F=0{\cdot}056$ for atomic aluminum and $R_F=0{\cdot}055$ for triply ionized aluminum which is necessary to account for the 6–9 bond length of 1·47 Å. Both calculations gave approximately 2·6 Al atoms (*versus* two for the stoichiometry) for the three partially filled sites. The assignment of triply ionized Al to the center of symmetry was considered unlikely since it would not be consistent with a minimum of charge transfer (Hoard & Hughes, 1967). Additionally, the carbon 9 distance of 1·467 Å was strikingly similar to the short B–C distance of 1·435 Å found in boron carbide. Therefore, a model with B at the center of symmetry was tested and similar complete refinement gave $R_F=0{\cdot}053$. Atom 9 was considered to be boron, but the presence of some carbon could not be excluded.

A model of the nine atom structure showed holes large enough to accommodate additional atoms, probably aluminum; hence, a difference Fourier based on signs determined from all B and C atoms was calculated. Two large maxima corresponding to atoms 7 and 8 were observed; in addition, two extremely small peaks within the holes were detected at about the resolution of the map. These were all added as fractional Al reducing R_F to 0·050; one of these would not refine and was assumed false. The small real maximum added only 0·15 Al atoms to the unit cell. Other models to include the presence of C (Hoard & Hughes, 1967), Al (Lipscomb & Britton, 1960) or vacancies in the icosahedra

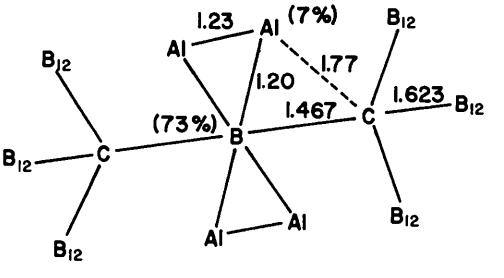


Fig. 1. Bond distances in the vicinity of the center of symmetry. $r_C=0{\cdot}77$ Å; $r_B\leq0{\cdot}9$ Å; $r_{Al}=1{\cdot}4$ Å.

Table 1. *Final atomic parameters**

	Type	Will†	x	$10^4\sigma_x$	y	$10^4\sigma_y$	z	$10^4\sigma_z$	B	$10^2\sigma_B$	Multiplier	$\sigma_{mult.}$	Fractional occupancies
1	B	B(5)	0·1615	3	0·0170	2	¾	–	0·4444	2	8	—	1·00
2	B	B(4)	0·3403	3	0·1805	2	¾	–	0·5076	2	8	—	1·00
3	B	B(1)	0	–	0·0467	2	0·4138	2	0·4412	2	8	—	1·00
4	B	B(2)	½	–	0·2492	2	0·5902	2	0·4341	2	8	—	1·00
5	B	B(3)	0·2543	2	0·1518	1	0·3480	1	0·4856	1	16	—	1·00
6	C	C	½	–	0·1529	2	0·4390	2	0·4135	1	8	—	1·00
7	Al	Al(3)	0·3175	12	0·0414	7	0·5524	7	0·4878	7	0·937	0·023	0·06
8	Al	Al(1)	0	–	0·2105	5	¾	–	0·3784	5	0·651	0·014	0·16
9	B	Al(2)	½	–	0	–	½	–	0·6446	3	3·67	0·04	0·92
10	Al	—	0	–	0·16	–	0·62	–	0·45	–	0·12	—	0·02

	β_{11}	$\sigma\beta_{11}$	β_{22}	$\sigma\beta_{22}$	β_{33}	$\sigma\beta_{33}$	β_{12}	$\sigma\beta_{12}$	β_{13}	$\sigma\beta_{13}$	β_{23}	$\sigma\beta_{23}$
1	31·5	2·9	14·8	1·2	13·6	1·1	−5·8	1·5	0	–	0	–
2	55·8	3·3	9·4	1·1	15·2	1·1	−1·0	1·6	0	–	0	–
3	41·3	2·9	13·0	1·2	11·8	1·1	0	–	0	–	1·1	1·0
4	32·6	2·7	13·4	1·2	13·9	1·2	0	–	0	–	−2·2	1·0
5	37·8	1·7	17·2	0·7	13·2	0·7	2·9	1·3	−2·4	1·0	−0·4	0·8
6	26·1	2·0	17·0	0·9	12·1	0·9	0	–	0	–	−3·8	1·0
7	50·9	11·7	6·2	4·0	16·1	4·3	−10·6	6·1	−6·3	6·6	1·6	3·7
8	23·0	7·8	11·2	3·5	13·9	3·3	0	–	0	–	0	–
9	44·7	4·6	21·9	2·1	22·4	2·0	0	–	0	–	1.4	1·8

* Atomic coordinates are in fractions of cell edges. Isotropic temperature factors and coordinates were taken from the 0·050 calculation. Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$ and were taken from the 0·043 calculation. Anisotropic temperature factors and errors have been multiplied by 10^4 for the tabulation.

† Atom designation given for C_4AlB_{24} by Will (1969).

Table 2. *Peak heights from* $R_F = 0{\cdot}050$ *Fourier**

	Type	Height	e.Å^{-3}	Site multiplicity	Apparent fractional occupancies
1	B(icosahedron)	2293	4·96	8	0·99
2	B(icosahedron)	2208	4·78	8	0·96
3	B(icosahedron)	2404	5·20	8	1·04
4	B(icosahedron)	2348	5·08	8	1·02
5	B(icosahedron)	2299	4·98	16	1·00
6	C	2780	6·02	8	1·00
7	Al	433	0·94	16	0·07
8	Al	1129	2·44	4	0·19
9	B	1697	3·67	4	0·73
10	Al	110	0·24	8	0·02

* 1 e.Å^{-3} was taken to be 1/5 the average height of atoms 1–5.

Table 3. *Interatomic distances* (Å)*

Atoms	Distance	Atoms	Distance
B–B intraicosahedral		3–7	2·204
1–1′	1·838	3–7′	1·993
1–3	1·840	3–10	1·867
1–5	1·823	4–7	2·145
2–2′	1·817	4–10	2·104
2–5	1·817	5–7	1·974
3–4	1·813	5–7′	2·133
3–5	1·823	5–8	2·060
4–5	1·784	5–10	2·194
2–5	1·817	6–7	1·768
5–5′	1·784	6–7′	2·015
		6–8	2·104
B–B intericosahedral		6–10	1·755
1–2′	1·773	7–9	1·200
3–3′	1·775		
B–C		Al–Al	
4–6	1·620	7–7′	1·204
5–6	1·625	7–7″	2·076
6–9	1·467	7–7‴	2·400
		7–10	2·189
B(C)–Al		8–10	1·236
1–7	2·017	10–10′	2·304
1–8	1·949		
1–10	1·946		
2–7	2·186		
2–8	1·955		
2–10	2·261		

* Only distances about equal to or less than the sum of the atomic radii are reported. Individual standard deviations can be calculated from the standard errors given for the coordinates and cell edges. The random standard error for B–B and C–B bond lengths is about 0·003 Å while those for Al–B and Al–C range up to 0·02 Å.

were tested by refining the multipliers of those sites, but no significant changes were detected. R_F remained at 0·050. Anisotropic refinement gave a final R_F of 0·043; however, such refinement is questionable for a structure with partially occupied sites. For completeness, the anisotropic temperature factors are given in Table 1.

A final three-dimensional electron density map was calculated from the $R_F=0{\cdot}050$ parameters; peak heights and atom assignments are shown in Table 2. With the assumption that the average B peak height corresponds to 5 e.Å^{-3}, the C position contains 6·02 e.Å^{-3}, confirming full occupancy at that site.

Table 4(*a*). *Observed and calculated structure amplitudes**

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
h=0			16 7	128	141	9 0	98	81	1 10	100	80	10 6	221	224	7 2	193	189	2 0	159	154	6 9	158	153
2 0	225	202	0 8	230	230	11 0	176	178	3 10	244	257	12 6	152	148	9 2	123	108	4 0	563	574	8 9	345	351
4 0	117	109	4 8	214	238	13 0	228	244	5 10	93	80	14 6	155	159	13 2	150	161	6 0	211	217	2 10	87	69
6 0	822	856	6 8	321	292	1 1	246	224	9 10	383	389	2 7	104	77	1 3	110	94	8 0	143	141	6 10	142	139
8 0	131	144	10 8	388	382	3 1	141	123	11 10	122	121	4 7	207	205	3 3	78	60	2 1	385	341	8 10	137	139
10 0	651	654	12 8	132	114	5 1	281	248	1 11	83	75	6 7	242	245	5 3	644	650	4 1	315	312	10 10	242	235
12 0	295	301	16 8	128	117	11 1	143	136	5 11	117	109	12 7	225	219	7 3	74	53	6 1	44	44	2 11	170	168
14 0	57	3	2 9	128	118	15 1	286	287	9 11	136	132	14 7	90	82	9 3	174	165	8 1	224	228	4 11	139	133
16 0	98	121	4 9	131	146	1 2	428	442	15 11	192	188	0 8	288	271	11 3	76	75	10 1	93	84	8 11	128	111
2 1	544	531	6 9	477	470	3 2	75	56	1 12	146	142	4 8	69	48	15 3	179	202	14 1	158	165	0 12	318	334
4 1	63	39	8 9	103	85	5 2	196	206	3 12	170	148	6 8	147	139	1 4	136	129	16 1	92	100	2 12	84	73
6 1	492	497	12 9	275	255	7 2	281	290	11 12	188	170	8 8	86	58	3 4	96	97	0 2	166	144	4 12	312	318
8 1	278	273	16 9	83	64	9 2	202	196	1 13	289	282	10 8	149	149	9 4	104	96	4 2	148	135	6 13	125	127
10 1	72	59	0 10	603	604	13 2	231	238	9 13	123	129	14 8	95	82	5 5	232	214	6 2	76	65	4 13	190	190
12 1	586	519	2 10	106	110	17 2	109	102	11 13	228	242	2 9	139	148	15 5	198	199	8 2	142	136	8 13	81	79
18 1	896	897	4 10	397	410	3 3	108	108	1 14	99	118	4 9	245	253	1 6	209	214	10 2	363	367	0 14	186	187
0 2	208	181	6 10	682	673	5 3	343	326	5 14	73	73	8 9	158	148	3 6	310	311	14 2	101	96	6 14	129	124
2 2	197	193	8 10	97	95	7 3	122	110	7 14	142	142	14 9	158	162	5 6	120	113	2 3	313	312	4 15	145	149
4 2	54	35	10 10	123	120	9 3	282	250	1 15	147	146	2 10	220	223	7 6	76	61	4 3	75	53	6 15	190	201
6 2	337	342	12 10	94	92	11 3	118	105	5 15	174	166	4 10	539	547	9 6	84	71	6 3	271	266	0 16	307	286
8 2	147	140	14 10	144	154	15 3	186	191	9 15	190	183	6 10	237	242	1 7	214	201	8 3	239	244	4 16	161	156
10 2	327	310	2 11	243	246	1 4	86	207	1 16	137	138	10 10	206	206	9 7	131	115	12 3	101	91	h=7		
2 3	1099	1090	4 11	135	123	3 4	66	3	3 16	96	94	14 10	269	257	11 7	193	201	0 4	488	499	1 0	102	96
4 3	354	343	6 11	337	357	5 4	57	39	9 16	147	147	2 11	443	436	1 8	82	62	2 4	163	47	3 0	311	313
6 3	239	254	8 11	230	243	9 4	194	181	1 18	177	180	4 11	211	204	3 8	173	164	4 4	121	108	7 0	169	153
8 3	496	508	12 11	398	401	13 4	73	51	1 19	162	156	6 11	78	79	7 8	114	97	6 4	555	574	11 0	147	158
14 3	114	131	14 11	101	88	17 4	110	96	h=2			8 11	398	415	9 8	70	55	8 4	122	117	13 0	134	136
2 4	395	391	0 12	708	718	1 5	100	79	0 0	415	388	12 11	115	118	11 8	95	95	12 4	133	131	1 1	127	133
4 4	424	434	4 12	245	254	3 5	72	43	2 0	74	54	0 12	255	253	13 8	96	95	14 4	147	141	3 1	74	57
6 4	286	304	6 12	203	195	5 5	240	251	4 0	557	545	6 12	123	125	1 9	166	164	2 5	310	290	11 1	135	129
8 4	124	106	10 12	103	95	9 5	120	110	6 0	432	454	8 12	78	82	5 9	326	317	4 5	164	156	15 1	184	189
10 4	660	643	12 12	136	116	15 5	290	290	8 0	108	107	10 12	208	214	9 9	175	174	6 5	378	384	1 2	146	138
16 4	146	134	14 12	97	71	1 6	254	295	10 0	116	102	4 13	326	147	1 10	117	112	8 5	278	279	5 2	113	95
2 5	477	471	2 13	232	239	3 6	509	546	14 0	120	113	6 13	186	179	3 10	174	174	10 5	75	71	7 2	228	228
4 5	286	294	4 13	304	317	5 6	130	146	16 0	144	145	12 13	166	155	9 10	259	261	12 5	423	426	9 2	143	141
6 5	196	180	8 13	147	156	7 6	104	84	2 1	191	166	0 14	383	382	11 10	135	132	14 5	100	102	13 2	179	193
8 5	333	301	14 13	234	234	9 6	132	145	4 1	364	350	4 14	94	85	1 11	112	103	0 6	931	955	5 3	514	510
12 5	157	140	10 14	235	237	11 6	102	79	6 1	260	296	6 14	289	294	5 11	162	147	2 6	173	174	7 3	98	100
14 5	159	155	2 15	369	323	13 6	82	83	8 1	237	237	10 14	121	115	9 11	95	91	6 6	282	277	9 3	183	185
0 6	728	739	6 15	167	172	1 7	279	287	10 1	110	97	2 15	123	116	1 12	115	111	10 6	395	410	11 3	84	74
2 6	51	84	8 15	266	268	3 7	68	60	12 1	95	92	0 16	249	233	3 12	104	95	12 6	107	108	1 4	109	107
4 6	521	552	2 16	110	114	9 7	110	97	14 1	116	112	h=5			11 12	142	128	14 6	85	70	3 4	113	106
6 6	141	135	6 16	226	232	11 7	258	259	0 2	1170	1148	3 0	315	308	1 13	213	214	2 7	75	58	9 4	161	158
8 6	157	143	10 16	234	226	15 7	169	170	4 2	74	32	7 0	299	313	9 13	131	127	4 7	182	189	1 5	79	57
10 6	100	79	2 17	141	129	1 8	97	77	6 2	383	406	11 0	95	90	11 13	158	152	6 7	91	84	3 5	93	82
14 6	356	345	4 17	131	123	3 8	150	166	8 2	170	170	13 0	212	226	1 14	87	90	12 7	104	117	5 5	164	159
16 6	140	135	0 18	188	178	11 8	138	143	10 2	250	249	5 1	262	242	7 14	122	116	2 8	101	97	9 5	151	157
2 7	369	390	4 18	157	156	11 8	109	127	12 2	252	252	7 1	64	41	1 15	114	119	6 8	261	259	1 6	166	165
4 7	457	434	h=1			13 8	130	141	2 3	291	266	11 1	67	63	5 15	126	121	8 8	123	112	3 6	424	431
8 7	221	222	3 0	847	805	1 9	156	156	4 3	178	182	15 1	208	217	1 16	113	116	10 8	354	350	5 6	82	79
12 7	106	93	5 0	69	48	5 9	463	458	6 3	190	170	1 2	205	196	h=6			2 9	421	426	7 6	92	80
14 7	230	236	7 0	336	361	9 9	254	242	8 3	122	112	5 2	154	151	0 0	729	740	4 9	119	109	9 6	142	132
10 3	69	52	6 12	284	280	11 4	88	76	7 15	92	82	13 6	92	84	6 7	108	103	5 11	190	189			
12 3	205	201	10 12	81	67	13 4	123	108	1 16	190	201	1 7	189	197	12 7	104	96	3 12	103	111			
14 3	118	109	4 13	121	118	1 5	363	382	3 16	125	130	11 7	172	169	0 8	106	86	h=10					
16 3	82	80	6 13	121	122	5 5	476	461	7 16	179	179	3 8	97	90	4 8	79	70	0 0	75	64			
18 3	190	191	12 13	114	105	7 5	205	192	11 16	117	112	7 8	137	135	10 8	108	115	4 0	175	176			
2 4	106	96	2 14	147	151	9 5	171	162	3 17	100	87	11 8	88	88	6 9	136	130	6 0	203	210			
4 4	383	402	4 14	139	126	11 5	181	185	5 17	125	114	1 9	65	46	8 9	147	127	10 0	109	115			
6 4	389	336	6 14	78	63	13 5	79	73	1 18	79	79	5 9	350	356	2 10	154	155	4 1	95	79			
8 4	115	94	10 14	88	75	17 5	105	114	3 18	150	155	9 9	155	162	4 10	344	348	6 1	131	141			
14 4	324	329	2 15	240	228	1 6	122	113	h=4			3 10	182	182	6 10	223	219	0 2	394	405			
16 4	168	169	4 15	229	229	5 6	121	125	0 0	1065	1068	9 10	173	201	8 10	257	257	6 2	199	209			
2 5	883	827	6 15	177	165	7 6	320	315	2 0	298	290	11 10	86	95	4 11	114	103	8 2	50	43			
4 5	264	265	8 15	222	213	9 6	159	147	4 0	200	188	1 12	109	100	8 11	248	253	10 2	122	115			
6 5	149	137	4 16	309	306	13 6	238	232	6 0	160	159	3 12	101	104	0 12	234	237	4 4	182	177			
8 5	714	715	6 16	275	278	17 6	155	152	8 0	225	234	1 13	214	206	4 12	93	87	6 4	98	86			
10 5	82	59	2 17	139	125	3 7	169	153	10 0	675	704	1 15	114	116	2 13	91	81	8 4	50	42			
12 5	251	252	4 18	124	110	5 7	390	375	12 0	149	158	h=8			4 13	105	109	2 5	317	326			
14 5	217	234	h=3			9 7	445	434	14 0	186	178	0 0	675	677	0 14	200	198	4 5	159	164			
0 6	686	722	1 0	95	60	1 8	172	171	16 0	148	172	2 0	203	193	h=9			6 5	69	55			
2 6	403	419	3 0	137	151	3 8	710	713	2 1	562	576	4 0	122	107	1 0	97	81	8 5	297	306			
4 6	230	236	7 0	509	544	7 8	65	25	4 1	179	172	6 0	183	177	7 0	320	325	0 6	249	238			
6 6	79	61	9 0	345	330	9 8	242	237	8 1	538	535	8 0	130	143	9 0	105	110	2 6	152	148			
8 6	682	680	11 0	114	119	1 9	328	323	10 1	73	53	10 0	398	417	1 1	113	110	4 6	111	105			
10 6	164	164	13 0	395	389	3 9	157	162	12 1	93	95	12 0	138	151	5 1	280	292	6 6	55	56			
2 7	159	136	15 0	87	64	5 9	218	216	14 1	152	155	2 1	295	296	7 1	85	74	2 7	93	94			
6 7	88	67	17 0	118	116	9 9	70	64	0 2	514	532	4 1	85	63	9 1	144	143	6 7	90	87			
8 7	205	192	1 1	235	207	11 9	144	148	2 2	172	167	6 1	73	52	3 2	279	288	0 8	247	250			
12 7	76	47	3 1	125	117	15 9	298	300	4 2	243	232	8 1	297	304	5 2	125	129	4 8	71	61			
0 8	353	350	5 1	456	469	1 10	123	115	6 2	202	200	12 1	117	119	3 3	147	148	6 8	138	145			
2 8	104	110	7 1	146	134	3 10	178	170	8 2	83	72	0 2	192	188	5 3	231	223	2 9	129	117			
4 8	206	209	9 1	359	354	5 10	105	79	12 2	153	158	2 2	81	60	9 3	296	309	0 10	259	269			
6 8	218	215	11 1	75	64	7 10	157	145	14 2	98	94	4 2	113	104	1 4	142	138	h=11					
10 8	270	272	13 1	82	79	11 10	168	150	16 2	99	85	6 2	65	52	7 4	296	309	3 0	71	59			
16 8	93	93	3 2	746	736	3 11	95	88	2 3	310	323	8 2	92	76	7 4	101	83	7 0	85	99			
2 9	347	338	5 2	135	132	5 11	268	266	8 3	212	212	12 2	87	92	9 4	89	85	1 1	79	76			
4 9	70	46	7 2	78	66	7 11	87	70	12 3	332	336	2 3	272	265	1 5	119	112	5 1	81	80			
8 9	252	244	9 2	112	93	9 11	128	120	0 4	622	657	8 3	220	212	3 5	204	203	3 2	71	61			
12 9	282	281	11 2	183	172	11 11	133	139	2 4	128	133	12 3	165	169	5 5	104	114	5 2	64	60			
0 10	627	627	13 2	133	139	3 12	271	273	4 4	95	94	0 4	328	325	7 6	71	69	7 2	105	97			
2 10	76	71	1 3	331	331	7 12	180	185	6 4	223	209	2 4	92	83	9 6	189	185	1 3	56	55			
4 10	148	141	3 3	352	353	9 12	229	228	10 4	379	383	4 4	80	70	11 6	99	94	5 3	242	251			
6 10	169	157	5 3	356	347	11 12	85	66	12 4	135	127	10 4	261	274	1 7	68	57	1 4	82	84			
8 10	109	122	7 3	109	98	13 12	112	115	14 4	126	106	4 5	146	147	5 7	143	152	1 5	88	83			
10 10	237	235	9 3	179	177	1 13	141	132	16 4	169	153	6 5	124	125	9 7	230	233	5 5	181	177			
12 10	134	128	11 3	146	135	3 13	112	102	4 5	241	226	0 6	73	47	1 8	75	70	3 6	165	159			
4 11	121	114	15 3	415	425	5 13	196	187	6 5	90	66	2 6	97	89	3 8	332	341	1 7	67	63			
6 11	158	140	1 4	367	344	9 13	353	350	12 5	205	200	4 6	170	166	5 8	128	127						
12 11	115	113	3 4	530	568	11 13	98	96	0 6	136	140	6 6	267	271	1 9	176	186						
0 12	112	111	5 4	62	44	3 14	253	255	4 6	254	238	10 6	130	122	5 9	93	84						
2 12	80	64	7 4	267	265	9 14	88	78	8 6	541	545	12 6	77	60	1 10	122	115						
4 12	312	310	9 4	135	130	1 15	270	280	8 6	66	42	2 7	116	105	7 10	122	121						
												4 7	150	145	1 11	157	152						

* Calculated from the $R_F=0{\cdot}050$ parameters. Scattering curves for B, C and Al were obtained from *International Tables for X-ray Crystallography* (1962). The final scale factor, by which F_{calc} is multiplied to place it on the observed scale is 1·023.

Table 4(*b*). *Unobserved* and calculated structure amplitudes*

		F_c
h=0		
18	0	50
14	1	37
16	1	10
12	2	46
14	2	17
16	2	11
18	2	33
10	3	23
12	3	9
16	3	37
18	3	53
0	4	47
12	4	4
14	4	49
18	4	36
10	5	31
18	5	75
12	6	33
6	7	34
10	7	47
2	8	60
8	8	25
14	8	18
10	9	55
14	9	77
10	11	55
2	12	7
8	12	56
6	13	45
10	13	38
12	13	46
0	14	43
2	14	30
6	14	56
8	14	81
12	14	36
4	15	34
10	15	25
0	16	40
4	16	40
8	16	53
6	17	38
8	17	83
2	18	2
6	18	29
2	19	34
h=1		
1	0	54
15	0	9
17	0	16
7	1	20
9	1	18
13	1	52
17	1	8
11	2	4
15	2	39
1	3	55
13	3	39
17	3	65
7	4	24
11	4	35
15	4	8
7	5	9
11	5	18
13	5	29
17	5	20
15	6	50
17	6	29
5	7	2
7	7	1
13	7	51
17	7	21
5	8	8
9	8	11
15	8	33
3	9	34
7	9	51
11	9	1
13	9	24
15	9	81
7	10	5
13	10	35
15	10	80
3	11	21
7	11	6
11	11	22
13	11	5
5	12	2
7	12	59
9	12	58
13	12	59
3	13	37
5	13	36
7	13	24
13	13	36
3	14	33
9	14	73
11	14	10
3	15	11
7	15	4
11	15	55
5	16	25
7	16	71
1	17	15
3	17	7
5	17	36
7	17	21
3	18	63
5	18	54
h=2		
12	0	24
18	0	15
8	1	14
10	1	14
2	2	32
14	2	23
16	2	19
18	2	8
0	4	72
10	4	5
12	4	57
16	5	54
6	6	53
12	6	42

		F_c
14	6	39
4	7	46
10	7	20
14	7	8
16	7	22
8	8	12
14	8	5
6	9	37
10	9	6
14	9	2
16	9	13
14	10	76
2	11	29
8	11	40
10	11	1
14	11	14
8	12	30
12	12	69
14	12	99
2	13	24
8	13	19
10	13	6
0	14	64
8	14	10
12	14	21
10	15	39
0	16	82
2	16	72
8	16	38
4	17	61
6	17	24
0	18	23
2	18	2
h=3		
5	0	24
15	1	42
17	1	77
15	2	29
17	2	32
13	3	14
17	3	21
15	4	28
17	4	46
3	5	32
15	5	6
3	6	5
11	6	20
16	7	11
1	7	51
7	7	8
11	7	39
13	7	70
15	7	59
5	8	41
11	8	29
13	8	72
15	8	35
7	9	22
13	9	2
9	10	24
13	10	80
15	10	27
13	11	29
1	12	13
5	12	21
7	13	18
1	14	3
5	14	52
7	14	0
11	14	52
3	15	36
5	15	29
9	15	38
5	16	28
9	16	16
7	17	9
h=4		
6	1	29
16	1	29
10	2	43
4	3	18
6	3	25
10	3	23
14	3	23
16	3	33
8	4	10
16	4	37
2	5	23
10	5	5
14	5	27
16	5	58
16	6	57
8	7	12
10	7	8
16	7	68
2	8	29
12	8	67
10	9	50
12	9	46
0	10	18
8	10	4
12	10	15
10	11	47
2	12	38
4	12	90
12	12	'9
2	13	57
8	13	10
10	13	14
2	14	33
8	14	32
4	15	24
6	15	21
8	15	76
2	16	34
4	16	72
6	16	2
8	16	12
2	17	2
4	12	27
0	18	32
h=5		
1	0	86
5	0	44
9	0	70

		F_c
15	0	15
1	1	21
3	1	34
9	1	11
13	1	40
3	2	21
11	2	4
15	2	20
13	3	35
5	4	29
7	4	3
11	4	8
13	4	58
15	4	2
1	5	30
3	5	17
7	5	6
9	5	22
11	5	3
13	5	15
11	6	57
13	6	76
15	6	37
3	7	44
5	7	12
7	7	21
13	7	40
15	7	96
5	8	7
15	8	36
3	9	36
7	9	25
11	9	30
13	9	21
5	10	51
7	10	37
13	10	7
3	11	9
7	11	21
11	11	51
13	11	5
5	12	9
7	12	68
9	12	69
3	13	25
5	13	25
7	13	4
3	14	29
5	14	55
9	14	32
3	15	11
7	15	3
3	16	44
5	16	18
1	17	22
3	17	11
h=6		
6	0	20
8	0	2
10	0	21
12	0	42
10	1	4
2	2	17
12	2	30
16	2	87
10	3	3
14	3	39
8	4	8
8	6	4
8	7	5
10	7	11
14	7	94
0	8	24
8	8	10
12	8	35
14	8	57
10	9	8
12	9	15
0	10	50
4	10	41
12	10	43
6	11	72
10	11	9
12	11	90
6	12	3
8	12	9
10	12	39
6	13	10
2	14	49
4	14	6
8	14	17
2	15	55
2	16	4
h=7		
5	0	19
9	0	43
15	0	2
5	1	46
7	1	7
9	1	24
13	1	28
3	2	50
11	2	15
15	2	31
1	3	31
3	3	40
13	3	30
5	4	28
7	4	12
11	4	16
13	4	27
7	5	44
11	5	14
13	5	25
11	6	58
3	7	49
5	7	21
7	7	21
9	7	41
13	7	32
1	8	50
5	8	7
9	8	12
3	9	13
7	9	51

		F_c
11	9	34
1	10	16
5	10	43
7	10	37
11	10	46
1	11	11
3	11	25
5	11	28
7	11	6
5	12	1
7	12	8
9	12	26
3	13	24
5	13	28
7	13	33
1	14	63
3	14	62
5	14	39
3	15	31
h=8		
10	1	18
10	2	57
4	3	4
6	3	46
10	3	9
6	4	55
8	4	30
12	4	54
2	5	37
8	5	32
10	5	18
12	5	[illegible]
8	6	26
8	7	49
10	7	9
2	8	42
6	8	47
8	8	4
2	9	55
8	9	58
10	9	21
0	10	46
8	10	7
6	11	75
2	12	10
6	12	39
2	14	18
h=9		
5	0	21
3	0	20
11	0	22
3	1	30
11	1	70
9	2	57
7	2	24
5	2	44
11	2	77
7	3	53
11	3	53
5	4	23
11	4	31
3	5	38
7	5	67
11	5	74
3	6	45
5	6	46
3	7	68
7	7	1
5	8	17
7	8	1
3	9	71
7	9	15
3	10	36
5	10	22
3	11	29
1	12	6
h=10		
2	0	2
8	0	45
2	1	7
8	1	30
10	1	2
2	2	25
4	2	23
2	3	40
4	3	66
6	3	5
8	3	26
0	4	64
2	4	35
8	6	42
4	7	22
2	8	[illegible]
4	9	9
2	10	6
h=11		
1	0	11
5	0	7
1	1	43
3	1	1
7	1	9
3	3	32
3	4	17

* All unobserved structure amplitudes have a value of 25, approximately one-half the value of the lowest observed structure amplitude.

Site 9 gives 2·94 B atoms, while 7 and 8 yield 1·15 and 0·75 Al atoms respectively. This nine-atom structure then leads to the stoichiometry $C_8Al_{2\cdot0}B_{51}$ which increases the calculated density of 2·42 g.cm^{-3} for C_4AlB_{24}, $Z=2$ to the more agreeable value 2·52 g.cm^{-3}. Inclusion of the extremely small peak (10) yields $C_8Al_{2\cdot15}B_{51}$ and a calculated density of 2·53 g.cm^{-3}. Our empirical formula therefore, is quite close to $C_8Al_2B_{52}$, the stoichiometry of the ideal ternary compound of Hoard & Hughes.

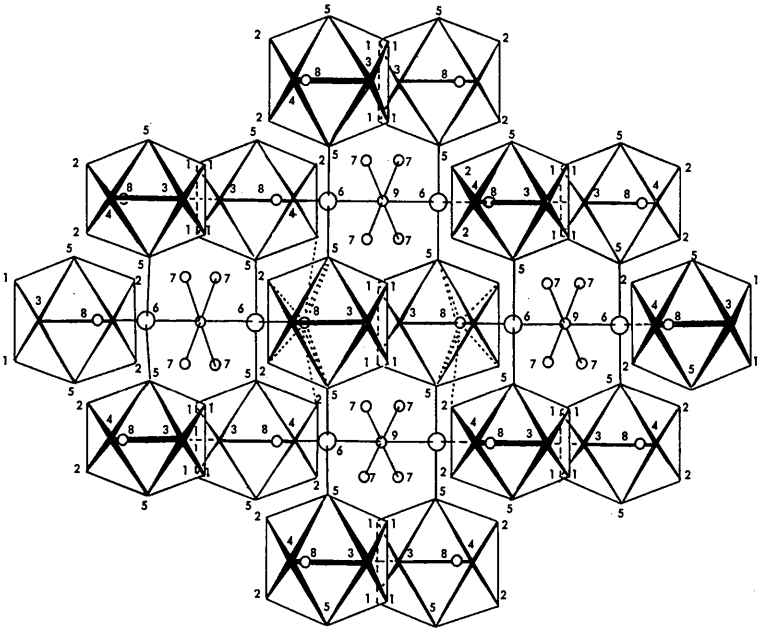
Discussion

Final atomic coordinates, isotropic temperature factors and atom multipliers from the $R_F=0{\cdot}050$ data are shown in Table 1. It should be noted that the temperature factors of the B atoms are reasonable and self-consistent. Interatomic distances are given in Table 3. Observed and calculated structure amplitudes are shown in Table 4.

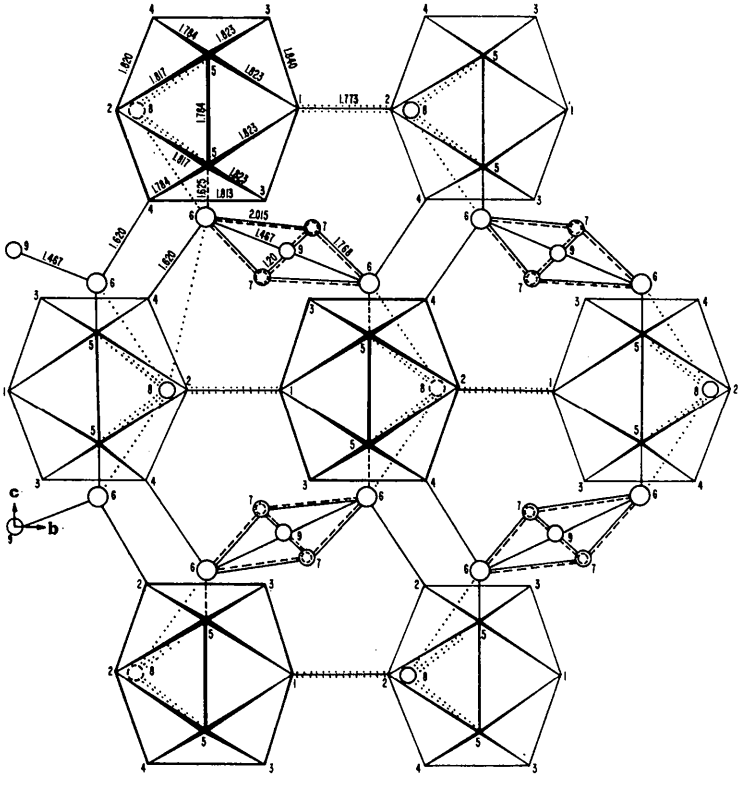
The crystal structure, viewed along the *a* and *c* axes (Fig. 2), clearly reveals distorted hexagonal close packing of B icosahedra. Sixfold coordination about each icosahedral B atom is completed by C in two symmetry-distinct instances and by a B atom from an adjacent icosahedron in the remaining two cases. Thus, six of the icosahedral B atoms form B–B bonds and six form B–C bonds. Boron atoms on a partially occupied center of symmetry complete a tetrahedral environment for C (Table 5) and develop linear C–B–C chains similar to those found in rhombohedral boron carbide. In addition, C links three icosahedra to form a three-dimensional network. This type of bonding is reminiscent of that found in boron carbide; the analogy is enhanced by a comparison of bond distances for the two structures (Table 6). All B–B and B–C bonds in $C_8Al_{2\cdot1}B_{51}$ are only 0·02 to 0·05 Å longer than those in boron carbide, supporting the suggestion (Hoard & Hughes, 1967) that this ternary phase is in fact an aluminum stabilized twinned derivative of the more simple boron carbide. The suggestion is strengthened further by the observation that 'C_4AlB_{24}' undergoes a topotactic transition with loss of Al at about 2000 °C to the boron carbide structure (Giese, Economy & Matkovich, 1966). This type of transition now seems reasonable since similar intericosahedral bonding exists for both structures; however, the details of the mechanism are still not entirely clear. Use of the stoichiometry C_4AlB_{24} (Matkovich, Economy & Giese, 1964; Will, 1969) with C–Al–C chains does not lead to as direct an interpretation of this transition.

Table 5. *Tetrahedral angles about carbon*

Atoms	Angle
4–6–5	115·8°
4–6–9	99·6
5–6–5′	118·7
5–6–9	100·8



(*a*)



(*b*)

Fig. 2. (*a*) The crystal structure of $C_8Al_{2\cdot1}B_{51}$ as viewed along *d*(001). (*b*) As viewed along *d*(100).

Table 6. *Comparison of average bond distances between* $C_8Al_{2\cdot1}B_{51}$ *and boron carbide*

Bond type	$C_8Al_{2\cdot1}B_{51}$	Boron carbide*
B–B(icosahedral)	1·816	1·789
B–B(intericosahedral)	1·774	1·718
B(icosahedron)–C	1·623	1·604
B(chain)–C	1·467	1·435

* Values taken from Hoard & Hughes, 1967.

Questions as to the stabilizing role of Al now arise quite naturally. As stated earlier, all Al atoms are on partially occupied sites in vacancies between icosahedra. One of these atoms competes statistically with the B atom of the C–B–C– chain while the remaining Al atoms are irregularly coordinated to B atoms at distances ranging from 1·76 to 2·26 Å. All Al–B and Al–C nearest neighbor contacts are shorter than the sum of the covalent atomic radii by approximately 0·2–0·3 Å. Hence, whereas the boron and carbon framework is expanded with respect to boron carbide, aluminum is apparently in sterically forcing positions. At first, one might suspect that Al atoms contribute electronically to the stability of the structure by donating electrons. Such a view would be consistent with the approximate valence theory for boron carbide which predicts closed-shell B_{12}^{2-} icosahedra linked to $(C–C–C)^{2+}$ chains (Longuet-Higgins & Roberts, 1955); a slight modification, in accord with recent investigations, formally gives $B_{11}C^-$ icosahedra and $(C–B–C)^+$ chains with no loss of generality. For our structure with B_{12} icosahedra and C–B–C chains, the electron count is one short of satisfying the theory, suggesting a role for Al. However, the boron carbide of composition $B_{13}C_2$ which also contains B_{12} icosahedra and C–B–C chains, exists in the simple rhombohedral modification as an ordered chemical compound (Hoard & Hughes, 1967) and so arguments based on electron donor behavior for Al should be regarded with circumspectiom. The role of Al, be it dominated by steric, electronic, thermodynamic or kinetic considerations, will be understood completely only after more information becomes available.

For a thorough discussion of the boron-rich phases which treats many of the topics considered here more fully, the reader is referred to a recent review article (Hoard & Hughes, 1967).

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Die Struktur eines Phosphor(III,V)-Sulfids der ungefähren Zusammensetzung P_4S_9.

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P_4S_9 II crystallizes in space group *Ia*3 ($a = 17{\cdot}60$ Å). The molecules are very similar to the P_4O_9 molecule: 4 P atoms at the corners of a trigonal pyramid are linked by 6 S atoms; the remaining three S are terminal *S* atoms attached to 3 *P* atoms.

Einleitung

In der Literatur wurden die Strukturen von Phosphor–Schwefel-Verbindungen der Zusammensetzung P_4S_3 (van Houten, Vos & Wiegers, 1955; Leung, Waser, van Houten, Vos, Wiegers & Wiebenga, 1957), P_4S_5, P_4S_7 und P_4S_{10} (van Houten & Wiebenga, 1957; Vos & Wiebenga, 1955; Vos, Olthof, van Bolhuis & Botterweg, 1965) in zwei- bzw. dreidimensionaler Verfeinerung bereits eingehend beschrieben.

Meisel (1968) fand eine neue Phosphorsulfidphase der Zusammensetzung $P_4S_{8,5}$–P_4S_9, in der etwa 25% als