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The Structure Analysis of β-Rhombohedral Boron†

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A detailed discussion of the analysis of the structure of β-rhombohedral boron, β-B_{105}, is presented. Several formulations of the icosahedral framework structure are fully elaborated and detailed variations in bond lengths and bonding geometries are discussed. Perturbations of the ideal structure are effected through partial occupancies, substitutional atoms, and local disorders in framework and interstitial sites.

Introduction

Although detailed structure analyses have been reported for only three of the dozen or more proposed polymorphic forms of boron, evidence is steadily accumulating in support of the contention (*1*) that β-rhombohedral boron is the thermodynamically stable polymorph. The first structure to be determined was that of α-tetragonal boron or α-B_{50} (*2*, *3*). It now appears that this is a self-sustaining framework based upon a boride structure, MB_{25}. The complex framework is probably stable over the entire composition range M_xB_{25} with $0 \leqslant x \leqslant 1$. The second structure to be reported was the remarkably simple α-rhombohedral boron or α-B_{12} (*4*). It has been suggested (*1*) that this is a monotropic form of the element, stable only under specialized conditions. The third structure to be reported was that of β-rhombohedral boron or β-B_{105}; the basic structure was presented in a brief report (*5*) and was further amplified in subsequent discussions (*1*, *6*). The details of the analysis of this important structure are presented herein; none of the essential features of the structure given earlier are modified in this final formulation.

Experimental

Crystalline specimens of elementary boron of a stated purity of 99.4% were kindly provided by the Bell Telephone Laboratories through the courtesy of Dr. S. Geller. These had been prepared from rather pure amorphous boron supplied by Cooper Metallurgical Associates by crystallization from the melt under an atmosphere of helium in a Heliarc furnace. Other samples, specified as 99.5% pure boron, were kindly provided by the United States Borax and Chemical Corporation; data recorded from single crystal fragments from these fused pellets were used in the final structure analysis. This boron was prepared from the reduction of boric oxide with magnesium metal and subjected to a mixed fluoride flux at about 1000°C, after which most of the residual impurities were removed by vacuum sublimation at or near the melting point of boron (2250 ± 50°C). The difficulties involved in the preparation of purification of boron have been carefully explored in recent years (see, for example, *6*, *7*), and it appears that this procedure can yield the element at the stated level of purity if sufficient care is taken to exclude such tenacious contaminants as Al, Si, C, Mn, Fe, etc., at every stage of the preparation (*8*). In the present case, the impurity content was formally expressed in terms which correspond to addition of approximately ten magnesium atoms, three atoms of aluminum and one each of silicon, iron and manganese to the 8400 boron atoms of 80 unit cells. This is equivalent to an average of one-fifth of an impurity atom in each unit cell containing 105 boron atoms. Precise, quantitative determination of the detailed impurity concentrations in such a system is, at best, a difficult analytical task; nevertheless, utilizing the basic boron framework structure reported herein as a standard, it is possible to assess the partial occupancy of interstitial and substitutional impurity sites from a detailed analysis of the diffraction data.

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This analysis (vide infra) suggests that the crystals used had somewhat higher impurity levels than was estimated by the supplier; no specific identification of impurities is possible, but magnesium and aluminum would appear to be the most likely metallic candidates.

Visual comparison of the X-ray diffraction patterns of crystals from these different preparations revealed no significant differences in the spacings, in the intensity distributions or in the character of the reflections beyond the minor variations associated with the uneven quality of different crystal fragments. There is little doubt, of course, that a detailed statistical treatment of all of the intensity data from the several crystals would reveal the small but systematic variations which must attend even minor differences in impurity concentrations. But, more to the point, there appears to be no reason to assume that the analysis of data even from an *ultra*pure sample would in any way vitiate the conclusions drawn herein about the basic three-dimensional framework of boron atoms; rather, we expect that the stability of the structure is such that it can accommodate a rather substantial concentration of specific impurities with only modest changes in bond lengths and local order.

The X-ray diffraction parameters derived from a careful analysis of CuKα data obtained on various samples on a General Electric XRD-3 spectrogoniometer were reported in an earlier communication (*9*) and the material was characterized as the β-rhombohedral polymorph of elementary boron. The rhombohedral lattice parameters are $a = 10.145 \pm 0.015$ Å and $\alpha = 65° \, 17' \pm 8'$ and the corresponding triply primitive hexagonal cell parameters are $a_h = 10.944 \pm 0.015$ Å and $c_h = 23.81 \pm 0.03$ Å.

The density of the material used in the structure analysis was determined to be 2.35 g/cc by a flotation measurement. If the primitive cell contained *only* boron atoms, the number, Z_B, would be determined by the density in the expression $Z_B = 45.87\ \rho$. Thus, the observed density would correspond to 108 boron atoms per unit cell; conversely, the basic framework described below involves only 105 boron atoms per repeating unit and would, therefore, correspond to an idealized crystal density of 2.29 g/cc. These observations are partially reconciled in a subsequent discussion of interstitial and substitutional solid solution in the boron framework.

In the absence of any systematic extinctions, the observed diffraction symmetry of the rhombohedral lattice was compatible with any one of the three space groups, $R3m$, $R\bar{3}m$, $R32$. Statistical analyses of intensity distributions according to the formulations of Wilson (*10*) and of Howells, Phillips, and Rogers (*11*) produced equivocal results which were readily attributable to a hypercentric distribution and pseudosymmetry after the structure was solved. The distribution of peak density in Patterson space (*12*) was not inconsistent with $R\bar{3}m$ and a sensitive capacitance measurement in a varying field failed to detect the slightest piezoelectric signal. Thus, understandably, the choice inevitably devolved to the centrosymmetric space group $R\bar{3}m$; the results of the structure analysis fully support this assumption, post facto.

Integrated intensities were measured on the spectrogoniometer from a stationary crystal with converging beam geometry. A diffractometer take-off angle of 7° ensured that a reasonable mosaic angle was subtended by the source focal spot at every point on a crystal of over-all dimensions of 0.15–0.20 mm. After preliminary scanning to screen out very low level or absent reflections, peak intensities were recorded on a fixed count basis with a krypton filled proportional counter. Background corrections were evaluated from the systematic application of carefully calibrated, balanced Ross filters to each peak intensity measurement. For Mo Kα radiation, these filters were prepared from zirconium foil and from homogeneous films fabricated from yttrium oxide and binders; nickel-cobalt filters were used for Cu Kα radiation.

An empirically determined linear interpolation correction was applied as a function of angle to account for the Kα_1–Kα_2 dispersion observed with both copper and molybdenum radiation. No corrections were applied either for extinction or absorption; the latter is utterly negligible and the former is at best, uncertain in a structure of this hardness and complexity. It would be appropriate to consider the difficult question of extinction corrections in any future elaborate refinement of data from an ultrapure crystal. Standard polarization factors were applied and Lorentz factors were used to account for the equivalent quasirotation through the mosaic angle in the converging beam.

All reflections accessible in the full 2θ range of the spectrogoniometer were measured with Cu Kα radiation. The range of these measurements was extended with Mo Kα radiation and the data sets were combined in a very satisfactory statistical cross-calibration of overlap measurements. This procedure yielded a total of 1445 reflections. As a result of the small size of the crystal, a falloff in quality of these data with increasing angle was evident and, in the final refinement of the structure, an arbitrary cutoff was applied at $2\theta \leqslant 70°$ (Mo Kα); this circumscribed a total of 921 reflections in a volume approximately twice that of the Cu Kα sphere in reciprocal space.

Discussion of the Analysis

A three-dimensional Patterson function was calculated and, predictably for a structure with more than one hundred identical atoms per unit cell, was not subject to unambiguous interpretation. Nevertheless, ill defined concentric shells of density, while not definitive, were consistent with the presence in the structure of icosahedra of boron atoms. The unique role of this extraordinary structure element in the crystal chemistry of boron and the higher borides had already begun to emerge from a consideration of the icosahedral structures of boron carbide (*13*) α-tetragonal boron (*2, 3*) and α-rhombohedral boron (*4*). Moreover, the basic metrics and characteristic angles of this structure element were imbedded in the pseudocubic geometry of the β-rhombohedral lattice in a way which suggested some complex stellation or tessellation of the boron carbide framework structure.

A systematic application of direct statistical methods was clearly indicated and a subsequent extension of early results did indeed ultimately lead to the correct structure (*14*). However, at an early stage, the analysis suddenly yielded to a framework model which was derived from a stereochemical analysis of boron bonding. The framework was based upon the union of complex 84-atom structure elements which (in slightly idealized form) displayed full icosahedral symmetry and which played a role analogous to that of the icosahedron in the boron carbide structure. Fourier syntheses based upon this B_{84} unit quickly revealed additional atoms and the full framework of 105 atoms emerged from a systematic iteration of Fourier and least-square analyses (*5*).

The final refinement was based upon a least-squares fit of the 921 independent reflections for which 2θ (MoKα) $\leqslant 70°$. A total of 65 parameters, including coordinates, individual isotropic atomic

TABLE I

FINAL COORDINATES, TEMPERATURE FACTORS AND STANDARD DEVIATIONS FROM LEAST-SQUARES REFINEMENT OF 921 REFLECTIONS AT 2θ(MoKα) ≤ WITH CONVENTIONAL $R = 0.098$

B (*n*)	Hexagonal fractional coordinates x, y, z and standard deviations $\sigma_x, \sigma_y, \sigma_z$ ($x10^4$)						Isotropic temp. factor		Electron density[a]
n	x	σ_x	y	σ_y	z	σ_z	B (Å²)	α_B	e/Å³
1	0.1730	3	0.1742	3	0.1768	1	0.485	0.052	26
2	0.3189	3	0.2966	3	0.1291	1	0.538	0.053	23
3	0.2607	3	0.2172	3	0.4199	1	0.479	0.053	24
4	0.2351	3	0.2506	3	0.3473	1	0.624	0.054	23
5	0.0549	2	0.1097	2	−0.0560	2	0.551	0.062	31
6	0.0867	2	0.1735	2	0.0130	2	0.613	0.067	24
7	0.1091	2	0.2182	2	−0.1140	2	0.470	0.061	26
8	0.1703	2	0.3406	2	0.0281	2	0.623	0.064	21
9	0.1285	2	0.2570	2	−0.2338	2	0.569	0.064	27
10	0.1022	2	0.2044	2	−0.3020	2	0.348	0.062	25
11	0.0562	2	0.1125	2	0.3267	2	0.414	0.061	26
12	0.0894	2	0.1788	2	0.3990	2	0.353	0.062	27
13	0.0574	3	0.1148	3	−0.4460	2	0.780	0.088	17
14	0.0000	0	0.0000	0	0.3852	3	0.272	0.087	27
15	0.0000	0	0.0000	0	0.5000	0	1.315	0.160	20
16	0.0546	9	0.1093	9	0.1166	6	1.944	0.239	7

[a] Peak density is at nearest grid coordinate and is not the highest value at maxima.

Table II. Calculated and Observed Structure Factors for β-Rhombohedral Boron.

ℓ = 0

h	k	F_o	F_c
0	3	95	107
0	6	123	-112
0	9	287	350
0	12	483	506
0	15	364	-300
1	1	592	557
1	4	116	-98
1	7	282	-323
1	10	144	172
1	13	256	-335
2	2	849	-856
2	5	393	-386
2	8	194	-232
2	11	270	243
2	14	295	284
3	3	821	736
3	6	30	-23
3	9	52	-99
3	12	361	-349
4	4	1446	1278
4	10	310	-347
5	5	735	630
5	8	493	545
5	11	120	131
6	6	1861	1954
6	9	164	-232
7	7	722	710
7	10	104	82
8	8	609	548

ℓ = 1

h	k	F_o	F_c
0	2	1062	-1115
0	5	99	38
0	8	649	-744
0	11	232	-282
1	0	52	169
1	3	805	-777
1	6	650	695
1	9	147	122
2	1	698	693
2	4	391	385
2	7	212	-262
2	10	161	-136
3	5	1023	-1202
3	8	266	-277
4	0	1139	-1178
4	3	247	276
4	6	199	170
4	9	252	286
5	1	289	-345
5	4	177	-126
5	7	52	36
6	2	289	-338
6	5	140	163
6	8	501	-562
7	0	42	38
7	3	226	249
8	1	264	-342
8	4	375	-444
8	7	379	349
9	2	411	-457
10	0	519	503
10	3	317	-332
10	6	199	-140
11	1	189	191

ℓ = 2

h	k	F_o	F_c
0	1	461	288
0	4	1123	-1019
0	7	407	-418
0	10	185	-152
1	2	559	534
1	5	224	-246
1	8	187	-147
1	11	42	69
2	0	748	702
2	3	189	-212
2	6	73	81
2	9	411	436
3	1	580	547
3	4	99	72
3	7	218	237
3	10	264	255
4	2	279	-240
4	5	60	34
4	8	442	-433
5	0	310	269
5	3	1164	1220
5	6	30	-12
5	9	254	263
6	1	426	-435
6	4	206	-139
6	7	184	185
7	2	349	375
7	5	175	-163
8	0	318	-300
8	3	369	443
8	6	232	259
9	1	184	-171
9	4	189	189
10	2	430	-443
11	0	153	272
12	4	317	-311
14	0	224	188

ℓ = 3

h	k	F_o	F_c
0	0	1032	1183
0	3	284	-266
0	6	2063	-2168
0	9	52	19
0	12	480	418
0	15	112	40
1	1	615	566
1	4	30	-6
1	7	557	-565
2	2	571	613
2	5	99	-16
2	8	317	362
2	11	236	-229
2	14	298	294
3	0	622	-654
3	3	395	-357
3	6	203	-145
3	9	431	526
3	12	256	-250
4	1	164	-158
4	4	1463	1619
4	7	60	-66
5	2	131	-147
5	5	276	-256
5	8	539	646
5	11	517	-600
6	0	79	-90
6	3	140	127
6	6	79	-120
7	1	208	202
7	4	205	-191
7	7	295	340
7	10	127	-72
8	2	164	168
8	5	127	-117
8	8	442	471
9	0	232	210
9	3	116	-115
9	6	557	576
10	1	381	-367
10	4	271	278
10	7	334	-331
11	2	298	-317
12	0	140	91
13	1	397	-386
15	0	236	-154

ℓ = 4

h	k	F_o	F_c
0	2	918	848
0	5	30	39
0	8	216	124
0	11	359	357
0	14	123	241
1	0	1391	-1468
1	3	902	-810
1	6	647	692
1	9	374	-341
1	12	642	-702
2	1	542	410
2	7	393	-337
2	10	73	86
3	2	829	801
3	5	155	-162
3	8	243	-220
3	11	501	522
4	0	1061	-927
4	3	220	-230
4	6	226	234
4	9	42	16
5	1	352	-280
5	4	189	-137
5	7	389	-387
6	2	238	265
6	5	52	30
7	0	1044	-1069
7	3	90	100
7	6	585	-636
8	1	208	218
8	4	140	-111
8	7	521	508
9	2	214	254
10	0	635	-650
10	3	182	-216
11	1	189	174
13	0	276	278

ℓ = 5

h	k	F_o	F_c
0	1	788	798
0	4	323	-297
0	7	821	-807
0	10	742	-822
0	13	727	840
1	2	802	-780
1	5	90	-29
1	8	42	-21
1	11	1235	1328
2	0	363	-376
2	3	140	-92
2	6	270	-292
2	9	480	496
3	1	304	331
3	4	67	-46
3	7	180	-155
3	10	196	212
3	13	492	-525
4	2	270	-273
4	5	284	366
4	8	285	-301
4	11	393	-368
5	0	1160	1260
5	3	594	531
5	6	268	-291
5	9	317	-321
6	1	1384	1463
6	4	60	52
6	7	120	-128
7	2	158	176
7	5	134	138
7	8	495	536
7	8	495	536
8	0	338	-243
8	3	685	-760
8	6	509	-482
9	1	216	-251
9	4	177	-160
9	7	345	321
10	2	123	168
10	5	429	434
11	0	492	498
11	6	615	650
14	0	258	-244

ℓ = 6

h	k	F_o	F_c
0	0	1390	1148
0	3	956	931
0	6	458	483
0	9	140	-114
0	12	1368	1429
1	1	175	145
1	4	308	289
1	7	584	-677
1	10	85	104
1	13	287	215
2	2	535	-547
2	5	465	-509
2	8	85	-63
3	0	958	-826
3	3	417	-421
3	6	214	199
3	9	130	-163
4	1	205	-156
4	4	350	287
4	7	552	648
4	10	282	-284
5	2	449	503
5	5	116	115
5	8	127	136
6	0	1323	1359
6	3	666	-716
6	6	67	101
7	1	292	303
7	4	134	-135
8	2	282	-269
8	5	313	333
9	0	60	70
9	3	90	-113
9	6	307	-294
12	0	261	223
15	0	600	-547

ℓ = 7

h	k	F_o	F_c
0	2	637	578
0	5	709	-701
0	8	443	-400
0	11	645	669
0	14	104	-28
1	0	177	157
1	3	542	-527
1	9	205	168
1	12	273	-251
2	1	859	-788
2	4	153	140
2	7	143	-145
2	10	143	140
3	2	42	-30
3	5	314	295
3	8	660	-773
4	0	85	114
4	3	562	539
4	6	137	92
4	9	341	-386
5	1	85	74
5	4	552	-584
5	7	218	-262
6	2	220	210
6	5	192	-248
6	8	320	320
7	0	544	-657
7	3	212	191
7	6	350	425
8	1	192	-268
8	4	449	-503
8	7	299	-305
9	2	203	219
9	5	357	-369
10	0	340	311
10	3	95	-58
10	6	420	396
11	1	104	-106
11	4	454	-491

ℓ = 8

h	k	F_o	F_c
0	1	632	-626
0	4	104	-39
0	7	158	-239
0	10	67	2
0	13	632	692
1	2	414	358
1	5	364	-400
1	8	402	355
1	11	279	256
2	0	1022	-889
2	3	1185	1027
2	6	201	-232
2	9	347	344
2	12	134	214
3	1	108	70
3	4	1321	1354
3	7	120	147
3	10	430	458
3	13	344	326
4	2	158	-116
4	5	144	135
4	8	134	-130
4	11	348	-349
5	0	60	-3
5	6	680	-722
6	1	898	927
6	4	202	197
6	7	123	-169
6	10	344	-327
7	2	112	113
7	5	756	-870
7	8	449	432
8	0	515	491
8	3	252	-293
8	6	526	-551
8	9	559	544
9	1	454	465
9	4	112	117
9	7	411	414
10	2	254	-288
10	5	495	476
11	0	210	169
12	4	137	189

ℓ = 9

h	k	F_o	F_c
0	0	1536	1492
0	3	683	630
0	6	470	-517
1	1	668	-592
1	4	376	-377
1	7	134	-155
1	10	150	-172
2	2	123	-106
2	5	1001	-1096
2	8	67	-83
3	0	60	-26
3	3	301	327
3	6	189	187
3	9	203	-226
3	12	203	-145
4	1	386	-281
4	4	311	296
4	7	298	307
5	2	42	-47
5	5	52	-35
5	8	137	-149
6	0	1291	-1340
6	3	258	-232
6	6	67	-81
6	9	355	-343
7	1	177	122
7	4	563	-574
8	2	30	-48
8	5	264	269
9	0	564	608
9	3	363	413
10	1	871	-859
12	0	274	-345

ℓ = 10

h	k	F_o	F_c
0	2	247	-228
0	5	243	241
0	8	535	-282
0	11	167	-123
0	14	120	-35
1	0	299	328
1	3	462	-402
1	6	348	373
1	9	415	437
2	1	52	11
2	4	1699	1772
2	7	208	236
2	10	466	480
3	2	52	-66
3	8	325	-353
3	11	313	-292
4	0	697	-700
4	3	614	671
4	6	240	-289
4	9	311	-334
4	12	367	328
5	1	194	-217
5	7	60	-81
6	2	406	416
6	5	289	-287
7	0	439	-435
7	3	164	-268
7	6	194	236
8	1	203	-216
8	4	497	-477
8	7	373	378
9	2	52	-45
10	0	1536	1553
10	3	350	-340
11	1	631	718

ℓ = 11

h	k	F_o	F_c
0	1	428	-364
0	4	137	-128
0	7	401	508
0	10	203	-180
1	2	127	-66
1	5	1133	1194
1	8	402	-343
2	0	196	-219
2	3	120	-109
2	6	112	-96
2	9	302	298
3	1	457	-359
3	4	338	-411
3	7	404	-427
3	10	324	-274
4	2	481	-467
4	5	241	-174
4	8	286	319
5	0	630	689
5	3	299	296
5	6	164	218
6	1	42	12
6	4	218	-260
6	7	266	-261
7	2	167	-139
7	5	270	-251
7	8	341	-315
8	0	230	290
8	3	85	128
8	6	386	-342
9	1	131	-125
9	4	441	-427
10	2	726	-690
10	5	397	391
11	0	956	911
12	1	670	670
13	2	327	-302

ℓ = 12

h	k	F_o	F_c
0	0	610	546
0	3	341	-327
0	6	271	-275
0	9	212	-246
0	12	348	374
1	1	90	90
1	4	528	564
1	7	324	295
1	10	150	145
1	13	203	-144
2	2	414	-352
2	5	123	118
2	8	683	-622
3	0	656	-682
3	3	1001	-1008
3	6	85	81
3	9	203	164
4	1	714	722
4	4	208	208
4	7	52	-77
4	10	279	-253

Table II continued

h	k	F_o	F_c
5	5	73	101
6	0	323	-308
6	3	108	-109
6	6	108	121
7	1	251	232
7	4	104	-69
8	2	180	-165
8	5	328	-282
8	8	203	-164
9	0	565	-554
9	3	79	97
9	6	120	276
10	1	158	-150
10	4	419	-407
11	2	467	471
12	0	389	379
12	3	354	-365
ℓ = 13			
0	2	1192	1154
0	5	453	405
0	8	187	206
0	11	79	61
0	14	362	482
1	0	454	-496
1	3	112	95
1	6	278	193
1	9	234	-228
1	12	473	-441
2	1	52	45
2	4	1045	1157
2	7	104	-97
2	13	359	-322
3	2	169	223
3	5	355	351
3	8	539	550
4	0	1988	-2087
4	3	182	-152
4	6	616	613
5	1	520	-543
5	4	194	-225
5	7	435	-397
6	2	298	252
6	5	120	139
6	8	749	767
7	0	79	-79
7	3	336	-352
7	6	465	-458
8	1	245	-263
8	4	456	-412
9	2	149	170
9	5	335	310
10	0	953	928
10	6	370	-349
11	1	417	429
12	2	452	442
ℓ = 14			
0	1	617	-603
0	4	753	846
0	7	156	148
0	10	499	-534
1	2	164	-188
1	5	379	-326
1	8	210	201
2	0	429	-451
2	3	259	-303
2	6	180	-217
2	9	210	193
3	1	814	803
3	7	214	180
3	10	324	307
4	2	85	-116
4	5	252	237
4	8	99	88
5	0	444	-514
5	3	348	337
5	6	966	-1022
6	1	274	-207
6	4	240	-265
7	2	491	462
7	5	42	-80
8	0	30	15
8	3	331	-287
8	6	399	-424
9	1	120	115
9	4	293	279
10	2	164	88
11	0	674	-803
ℓ = 15			
0	0	95	-56
0	3	1256	1326
0	6	545	-656
0	9	104	-101
1	1	120	116
1	4	42	-45
1	7	403	-390
1	10	208	-240
2	2	504	-559
2	8	90	-81
2	11	331	-308
3	0	461	492
3	3	67	81
3	6	738	802
3	9	441	122
4	1	697	-757
4	4	208	137
4	7	172	186
5	2	167	-172
6	0	172	62
6	3	153	163
6	6	487	-523
7	1	187	-205
7	4	30	-16
8	2	90	-136
9	0	134	-160
10	1	99	112
12	0	387	-389
ℓ = 16			
0	2	1354	1480
0	5	362	-382
0	8	843	-896
1	0	587	355
1	3	636	623
1	6	313	270
1	9	203	195
2	1	399	-446
2	4	426	420
2	7	112	120
3	2	238	-222
3	5	292	-256
3	8	104	-131
4	0	791	-916
4	6	1423	1374
4	9	278	-264
5	1	104	74
5	4	515	-546
5	7	741	742
6	2	228	-236
6	5	120	124
6	8	430	414
7	0	445	441
7	6	402	407
8	1	52	-44
8	7	268	-243
9	2	664	77
10	0	341	371
10	3	296	299
11	4	361	312
12	2	214	115
ℓ = 17			
0	1	617	901
0	4	305	352
0	10	153	-105
1	2	1042	-1127
1	5	99	-98
1	8	108	150
2	0	273	-283
2	3	254	202
2	6	42	-56
2	9	112	-148
3	1	236	-231
3	4	254	228
3	7	909	-911
4	2	292	-275
4	5	367	-343
4	11	395	-340
5	0	488	470
5	3	131	-140
5	6	79	62
5	9	323	-307
6	1	222	-259
6	4	112	141
6	7	537	500
7	2	729	-745
7	8	368	-379
8	0	570	560
8	3	266	-279
9	1	79	-73
9	4	538	-519
11	0	471	563
ℓ = 18			
0	0	328	260
0	9	199	-261
0	12	172	-108
1	1	912	1027
1	4	108	101
1	7	359	-363
1	10	290	303
2	2	99	-70
2	5	340	-325
2	8	194	-180
3	0	180	-180
3	3	52	68
3	6	104	-108
3	9	228	195
4	1	232	-224
4	4	222	-230
4	7	1212	1204
5	2	483	501
5	5	844	840
5	8	318	306
6	0	549	-511
6	3	201	169
6	6	323	312
7	1	341	349
7	4	153	168
7	7	318	308
8	2	348	-301
8	5	412	381
9	0	299	279
10	4	208	-229
ℓ = 19			
0	2	177	182
0	5	95	93
0	8	274	-303
0	11	725	-772
1	0	401	-384
1	3	127	165
1	6	313	-326
1	12	443	-405
2	1	140	140
2	4	42	58
2	7	327	336
3	2	90	-84
3	5	42	7
3	8	388	364
4	0	457	-383
4	3	453	-443
4	6	228	-215
4	9	339	-318
5	1	462	-432
5	4	153	-122
5	10	238	179
6	2	361	367
6	5	150	-141
7	0	628	-639
7	3	161	-145
7	6	201	169
8	1	52	59
13	0	362	-423
ℓ = 20			
0	1	158	-110
0	4	42	-41
0	7	782	-791
1	5	434	-362
1	8	184	192
2	0	461	419
2	3	99	114
2	6	73	63
2	9	271	216
3	1	112	-96
3	4	570	612
3	7	539	-596
3	10	259	-192
4	2	67	81
4	5	240	258
4	8	828	836
5	0	299	-300
5	3	336	329
5	6	651	-673
6	1	339	-399
6	4	155	159
7	2	95	16
8	0	466	427
8	6	232	222
ℓ = 21			
0	0	603	-602
0	3	305	350
0	6	42	6
0	12	273	-268
1	1	79	99
1	4	226	-180
1	7	199	-198
1	10	341	280
2	2	140	150
2	5	546	-509
2	8	449	-392
3	0	73	80
3	3	236	-279
3	6	84	97
3	9	594	635
4	1	535	502
4	4	409	-428
4	7	562	593
5	2	332	332
5	5	236	282
6	0	359	-474
6	3	335	366
7	1	774	781
7	4	268	-207
8	2	314	301
10	1	612	-629
12	0	426	-455
ℓ = 22			
0	2	164	-202
0	5	299	294
0	8	192	-184
0	11	247	-260
1	0	123	117
1	6	73	56
1	9	447	-447
1	12	347	289
2	1	180	151
2	4	60	55
2	10	137	-67
3	5	108	-108
3	8	364	309
4	0	426	-431
4	3	659	-693
5	1	116	118
5	4	42	-43
5	7	299	-282
6	8	203	141
7	0	816	759
8	1	634	-701
8	4	339	-324
10	0	451	404
ℓ = 23			
0	1	99	106
0	4	940	1062
0	7	95	-106
0	10	746	851
1	2	240	205
1	8	495	-485
1	11	544	525
2	0	254	-302
2	3	446	-519
2	6	444	-431
3	1	230	-266
3	7	302	277
3	10	325	-299
4	2	639	633
4	5	73	20
4	8	386	352
5	0	391	388
5	3	90	107
6	1	836	793
6	4	349	-336
7	2	247	-205
8	0	671	695
8	3	548	-571
ℓ = 24			
0	0	30	-12
0	3	625	679
0	6	140	-175
1	1	287	-233
1	4	243	-133
1	7	134	-121
2	2	212	-196
3	0	440	494
3	3	42	-39
4	1	243	260
4	4	393	-445
6	0	468	588
7	1	220	169
8	2	325	290
10	1	230	-203
ℓ = 25			
0	2	158	164
0	5	1005	-1069
0	8	584	-614
0	11	414	-383
1	0	428	-409
1	3	210	261
1	6	175	-209
2	1	60	72
2	4	134	119
3	2	52	29
3	5	79	-74
4	0	841	-957
4	3	116	53
5	1	30	-43
6	2	504	-496
7	0	466	450
7	6	505	-488
11	1	167	-282
ℓ = 26			
0	1	287	-250
0	4	1161	1252
0	7	308	-297
0	10	112	44
1	2	134	-149
1	5	201	-149
1	8	535	529
2	0	471	-535
2	3	662	673
2	6	234	229
3	1	42	-21
3	4	30	44
4	2	338	394
4	8	216	198
5	0	79	95
5	3	428	448
6	4	673	-814
7	5	374	-365
8	0	1657	1708
ℓ = 27			
0	0	771	-805
0	3	1251	-1234
1	1	234	300
1	4	140	-172
2	2	99	140
3	0	144	-104
3	6	637	-645
4	1	60	-42
4	4	284	-239
6	0	254	-193
9	3	453	-476
ℓ = 28			
0	2	30	59
0	5	1192	1211
1	0	123	-92
1	3	95	105
1	6	571	561
1	9	194	-147
3	8	482	430
4	0	375	-404
4	3	274	-277
4	6	252	-191
5	1	279	217
ℓ = 29			
0	4	997	1076
0	7	324	282
1	2	218	-227
1	5	352	326
1	8	296	286
2	0	349	-387
3	1	73	65
3	7	284	-233
5	0	364	401
5	3	567	-547
ℓ = 30			
0	0	359	-330
0	6	588	593
1	1	137	-131
1	4	472	-535
3	3	624	584
4	1	316	-296
4	4	232	-218
8	2	230	169
ℓ = 31			
0	2	343	-347
0	5	379	448
1	3	711	758
2	1	357	340
2	7	601	612
5	1	683	-669
5	4	241	205
7	3	388	371
ℓ = 32			
0	1	541	-617
0	4	439	421
0	7	152	73
1	2	293	268
4	2	146	-201
ℓ = 33			
0	0	332	417
0	3	339	334
1	7	352	-311
3	0	790	-845
6	0	258	225
ℓ = 34			
0	2	153	-117
1	0	564	593
4	3	563	-547
ℓ = 35			
1	5	293	253
3	4	387	-323
5	0	199	-146
ℓ = 36			
1	1	293	232
2	2	398	438
ℓ = 38			
2	0	404	-430

temperature factors and a scale factor, were fixed by the analysis; coordinate relationships in special positions, assumed in the final refinements, reduced this number to a total of 51 independent variables in the least-squares analysis. This entirely satisfactory data-parameter ratio of 19 provided a conventional discrepancy index of $R = 0.098$ for the coordinates and temperature factors listed in Table I. The final values for the calculated structure factors are compared with the observed data in Table II. Utilizing the same set of coordinates in a calculation involving the total 1445 reflections observed out to 2θ (MoKα) $\approx 140°$, produced a value of $R = 0.129$. This rather reasonable increase in R was accompanied by an increase of almost 50% in the standard deviations of the atom coordinates; simultaneously, an average decrease of about 25% was observed in the atomic temperature factors and in their associated standard deviations.

As the refinement progressed, Fourier synthesis and difference syntheses were used to corroborate the least-squares analyses. It became apparent that an unusually high temperature factor ($B = 2.4$ Å^2) for atom B (*13*) could more plausibly be interpreted in terms of a partial occupancy of the site. It can be seen from the peak densities of the final Fourier syntheses reported in the last column in Table I that the B (*13*) site occupancy factor of two-thirds used in the final least-squares analysis was entirely appropriate. Moreover, the corresponding temperature factor is more reasonable in terms of structural constraints which will be discussed below. Similarly, a second major site of partial occupancy lies at B (*16*); consistent with the low Fourier peak density recorded for this atom in Table I, an occupancy factor of one-third was used in the final least-squares analysis. The relatively high temperature factor suggests that there is residual structural disorder in this local region or, possibly, some impurity concentration uncompensated in the atomic scattering factor. Finally, the high temperature factor and the slightly reduced peak density at B (*15*), while not sufficiently atypical to warrant a special occupancy parameter, suggest that this site is a vulnerable one.

The characterization of inherent disorders and of partial occupancies in framework sites and in interstitial sites in icosahedral framework structures is of fundamental importance, not only to the understanding of the disposition of impurity atoms in boron, but also to the development of detailed structural mechanisms of boride formation and indeed, to the study of the electronic properties of icosahedral bonding. Nevertheless, an essential point must not be obscured by the enhanced agreement which can be obtained by coupling Fourier analyses with least-squares refinements through site occupancy factors. Given a basic structure, the parameters which can be varied to improve the statistical agreement between the observed and calculated structure factors are strongly correlated. Essentially the same results can be achieved from any number of reasonable combinations of atomic form factors, atomic temperature factors and site occupancy factors. It is obvious that appropriate atomic scattering factors can be chosen only with an a priori knowledge of the detailed stoichiometry —information which is rarely available with any precision for the many impurity atoms that occur in boron and boride structures. Moreover, even if the impurity atom or the boride forming element is known or assumed, the stoichiometry can be deduced from the diffraction data only after further assumptions are made concerning the correlation between partial site occupancies and local disorder at or near the sites. It is clear that the number of degrees of freedom in such an analysis rises sharply when multiple sites and more than one kind of impurity atom are involved.

Each independent experimental constraint imposed upon such an analysis is of great value. In addition to precise measures of stoichiometry and density, one can contemplate the use of anomalous dispersion measurements in appropriate circumstances. Of greatest value would be a carefully calibrated series of single crystal studies on systems of continuously varying composition.

In icosahedral framework structures it is essential that a clear differentiation be made between framework and interstitial sites. In each case the framework must be specified in complete geometric detail as that irreducible connexity of covalent linkages which defines the ideal structure. This requirement so straightforward in such familiar structures as those of diamond, wurtzite, MB_6 and MB_{12}, involves surprisingly subtle issues in complex boron and icosahedral boride structures. This is due in part to the rather large holes which are bounded by the compact icosahedral groupings and, in part, to the anomalous (or, at least, ambiguous) role played by individual atoms or groups of atoms in filling in unique connexities in the structure. Simple examples of the latter would include the tetrahedrally bonded boron atom in the tetragonal α-B_{50} structure, the tetrahedrally bonded carbon atoms in boron carbide $(B_{11}C)CBC$ and the unique boron atom in the center of the cell in the present structure of β-rhombohedral boron. Most, but by no means all, framework atoms in the known structures are boron; the precise status of other elements may be difficult to determine, especially in systems displaying variable stoichiometry. For example, the exact role of aluminum in the family of boride and ternary borocarbide structures will require thoughtful consideration and careful argument.

It appears that many framework sites are subject to at least three kinds of structural perturbations. The first and simplest involves direct substitution of impurity atoms or boride forming elements for framework atoms in selected icosahedral and non-icosahedral sites. The arbitrary distinction drawn between the two kinds of substitutional atoms is purely operational; a substitutional (or interstitial) atom is deemed to be a boride forming atom when its location corresponds in some structurally significant way to its state in a known boride structure. Secondly, depending upon local bonding geometries and crystal growth conditions, some framework sites can exhibit partial occupancy, even in pure boron. Finally, certain framework sites are subject to structural disorder, especially those in the neighborhood of substituted sites and partially occupied interstitial sites.

In contrast to framework sites, interstitial sites are subject to the thermodynamically significant constraint that the lattice constants of the host phase are essentially unaltered by the inclusion of an interstitial component. It is clear that numerous holes in icosahedral framework structures are accessible to impurity atoms, to boride forming atoms and, as well, to extra boron atoms; moreover, partial occupancy of such sites is also to be expected. In addition, some of the holes are sufficiently large to provide more than one equilibrium position for the entrapped atom; the attendant statistical disorder serves to further mask the relationships between occupancy factors and atomic form factors in a detailed diffraction analysis.

The weight of the foregoing observations is largely anticipatory although some of the factors discussed were considered in detail in the analysis of the icosahedral structure of α-tetragonal boron (*3*). In the present analysis, only two site occupancy factors are involved; one characterizes partial occupancy of a site which is clearly in the framework (vide infra) and the other, of a site which is deemed interstitial. The analysis, which completely delineates the framework and explores the occupancy of all of the probable interstitial sites, extracts essentially all of the unequivocal information residing in the data. Nevertheless, it will be seen that a curious ambiguity remains in the interpretation of the crystal density. It is clear that in future it will be necessary to carefully expose all of the assumptions imbedded in diffraction analyses as, inevitably, detailed structural mechanisms are invoked to explain the extraordinary proliferation of boron polymorphs and nonstoichiometric icosahedral borides. These observations suggest that it would be useful to collect data from carefully annealed samples of the ultrapure boron now available in order to establish the electron density levels and temperature factors against which the state of impurities in quantitatively doped crystals might be calibrated. This program is underway, but in the absence of such data, the present analysis provides the basic structural framework and, as well, some measure of the sites at which localization of impurities and disorder might occur.

Discussion of the Structure

All of the essential elements of the structure deduced from the present analysis have been described in some detail elsewhere (*1*, *5*, *14*); for present purposes, a brief description will provide sufficient background for the presentation of all of the important bonding parameters.

A three-dimensional framework structure can be faithfully described in remarkably diverse but nevertheless complementary ways, each one of which illuminates different aspects of the structure. A description based upon the bonding geometry around each type of atom is often appropriate; alternatively, the corresponding space-filling coordination polyhedra can be used. Polyhedral constellations of atoms often reveal correlations among related structures in the various ways they link together or share vertices, edges and faces or, more subtly, in the ways they interpenetrate. Because the β-rhombohedral boron structure is moderately complex, it is useful to consider alternate descriptions based upon different building blocks. The present discussion will be restricted to linked arrays of three different icosahedral subunits, the B_{12} unit, the B_{84} unit and the B_{156} unit.

The simplest formulation of the β-B_{105} structure is provided by an analogy (*1*) to the well-known boron carbide structure, $(B_{11}C)(CBC)$. This rhombohedral structure, $R\bar{3}m$, is based upon a lattice which is approximately face-centered cubic; indeed, if the angle listed in Table III were 60°, the geometry, but not the symmetry, of the structure would be exactly FCC. The structure consists of a single icosahedron at each lattice point, oriented with a threefold axis along the rhombohedral direction; a linear CBC chain lies along the axis with the boron atom at the

TABLE III

RHOMBOHEDRALLY LINKED ICOSAHEDRAL FRAMEWORK STRUCTURES BASED UPON $R\bar{3}m$

	a (Å)	α	
B_{12}(1.80 Å)[a]	5.22	63° 26′	Hypothetical Structure
α-B_{12}	5.06	58° 4′	α-Rhombohedral Boron
(B_{11}C)(CBC)	5.17	65° 36′	Boron Carbide, B_4C
(B_{84})($B_{10}BB_{10}$)	10.14	65° 17′	β-Rhombohedral Boron, β-B_{105}

[a] Hypothetical rhombohedral framework structure of ideally linked perfect icosahedra of edge length 1.80 Å.

center of the cell and the carbon atoms near the interfaces between the central octahedral hole and the adjacent tetrahedral holes. The orientation of the icosahedra can be visualized by considering the hypothetical structure B_{12} (1.80) listed in Table III. Six of the 12 atoms in the perfectly regular icosahedron in this structure are in a very flat triangular antiprism which forms a slightly puckered (10° 50′) equatorial belt around the threefold axis. The remaining six atoms lie at the vertices of another triangular antiprism which interpenetrates the first. These vertices subtend at the center a rhombohedral vector triplet with $\alpha = 63° 26'$; bonding between adjacent icosahedra is effected radially along these rhombohedral directions to form a tight three-dimensional framework structure. This radial bonding along the quasifivefold axes of boron icosahedra generates the preferred pentagonal pyramidal coordination (*1*) around each boron atom. The remaining half of the atoms in this structure, the equatorial atoms, are too far apart to form a sixth bond in the preferred coordination geometry; in α-B_{12}, the angle collapses to 58° 4′ and the equatorial atoms from adjacent icosahedra link around the threefold axes in weak, triangular three-center bonds; in boron carbide, the equatorial atoms bond radially through the interposed carbon atoms on the ends of the central CBC chains.

The analogy between the β-rhombohedral boron and the boron carbide structures is revealed by reformulating β-B_{105} as (B_{84}) ($B_{10}BB_{10}$). The B_{84} unit is a quasispherical icosahedral entity which is centered at the lattice points of an approximately face-centered cubic rhombohedral lattice; the ($B_{10}BB_{10}$) chain lies along the threefold axis with the boron atom at the center of the cell and the compact B_{10} units near the interfaces between the central octahedral and adjacent tetrahedral holes. The B_{84} unit can be derived by stellating an icosahedron with 12 half-icosahedra; the six-atom pentagonal caps can be oriented to preserve full icosahedral symmetry for the whole unit. Alternatively, the unit can be derived by inserting two concentric icosahedra into the 60-atom shell pictured in Fig. 1. The 60-atom unit derives from the truncation of a regular icosahedron; each of the 12 vertices becomes a pentagon and each of the 20 triangular faces becomes a hexagon. The full B_{84} unit is depicted in Fig. 2.

The rhombohedral linkages between adjacent B_{84} units are effected through the juxtaposition of pentagonal caps rather than through the direct

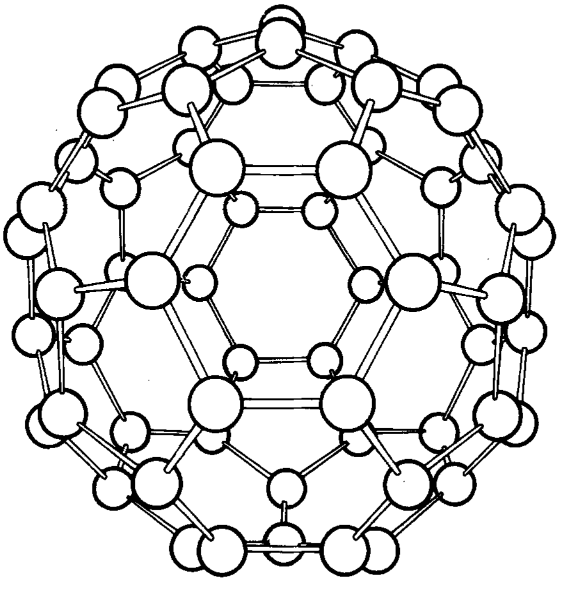

FIG. 1. A perspective view along the threefold axis of a 60-atom truncated icosahedron.

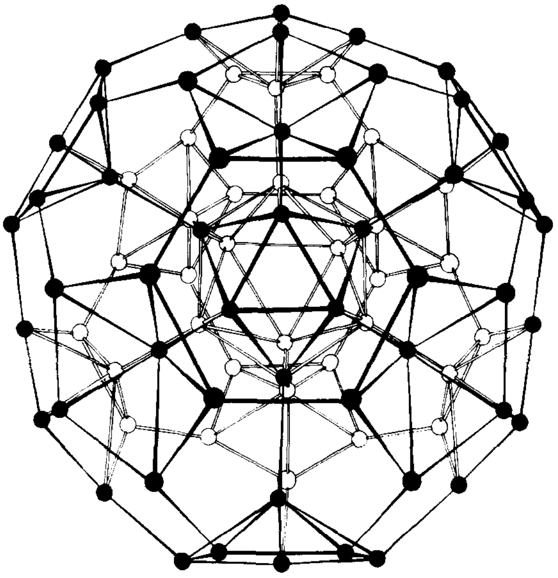

FIG. 2. A perspective view along the threefold axis of a B_{84} unit. Rhombohedral linkages between B_{84} units are effected through the juxtaposition of the half-icosahedra visible at the surface.

radial bonding found in the boron carbide structure. This juxtaposition produces, in each instance, a B_{12} icosahedron from the two half-icosahedra and thereby creates a framework structure with a high percentage of the preferred pentagonal pyramidal coordination.

The linkages between the equatorial pentagonal caps on adjacent B_{84} units are effected through the B_{10} units depicted in Fig. 3. When considered in conjunction with the three surrounding pentagonal caps this unit is clearly derived from the condensation of three B_{12} icosahedra around a threefold axis. One atom on the axis is shared by all three icosahedra, six other atoms are shared between pairs of icosahedra and the remaining three are unshared. These remarkable B_{10} units are linked through the boron atom at the center of the cell.

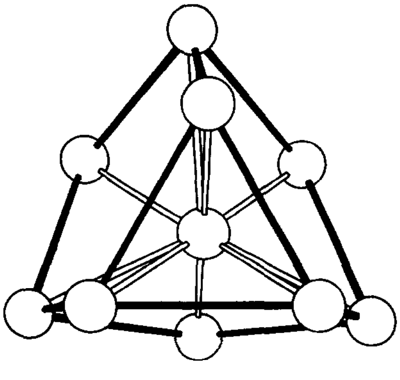

FIG. 3. The B_{10} subunit derived from the partial condensation of three icosahedra. Equatorial linkages between adjacent B_{84} units are generated through the pentagonal faces of this subunit.

An alternative description of the structure can be based upon the B_{156} unit derived by completely stellating the pentagonal faces of the B_{84} unit with half-icosahedron caps. This array of 12 B_{12} units around a central (slightly smaller) icosahedron displays full icosahedral symmetry. Placed at the lattice points of the rhombohedral cell it completely reproduces the entire structure, except for the single boron atom at the center of the cell. The rhombohedrally directed icosahedra between adjacent B_{156} units overlap completely and identically; the equatorially directed icosahedra overlap partially to form the B_{10} units described above. Other connexities between B_{156} units are of interest in higher boride structures.

Emphasis can be placed upon B_{12} units in another description of the structure based upon linear chains of icosahedra radially bonded along quasifivefold axes coincident with the rhombohedral cell axes. In each chain, adjacent icosahedra are related by a rotation of $2\pi/10$ and a translation of $a/2$. The large holes in this rhombohedrally linked framework are filled by the B_{28} unit derived from the partial condensation of three icosahedra around the threefold axis. This, of course, is the B_{10} unit with three half-icosahedra added to its three pentagonal faces.

It should be emphasized, in every case, that the compact quasispherical structural units link together in a strong three-dimensional covalently bonded framework. This combination of compact units and strong, directed covalent bonding creates a structure with many holes; in the B_{84} unit, for example, each of the 20 hexagonal faces caps a truncated tetrahedron which is large enough to accommodate an extra atom; and even larger holes exist between the units. The distribution of extra boron atoms and other impurity atoms in these holes undoubtedly contributes to anomalies observed in the density of the crystal. Occupancy of selected sites also provides the driving force for the formation of related boride structures.

None of the icosahedral structural units described above are perfectly regular, but the distortions which do occur are modest, and it is convenient to preserve the concept of regular icosahedral symmetry in all general descriptions of the structure. Nevertheless, a careful study of the deviations which do occur is essential in any analysis of the relationships among boron and boride structures.

The central icosahedron in the B_{84} units located at the origin is very nearly regular. The slight distortion which does occur involves a constriction around the equatorial belt where the average bond length is 1.75 Å (B6–B6). The rhombohedral atoms, B5, are bonded at 1.80 Å and the over-all average bond length is 1.767 Å.

The icosahedra located at the mid-edges of the cell involve atoms B1, B2, B7, and B9. These are nearly regular with an average bond length of 1.85 Å; however, the B1–B1 bond is substantially longer than the average at 1.92 Å. In the B_{84} unit, this bond is in the hexagon at the poles through which the threefold axis passes. The remaining (B1–B1, intericosahedral) link in this hexagon is also unusually long (1.88 Å). This dilation is a magnification of the distortion observed in the central icosahedron. The rhombohedrally directed intericosahedral bond between icosahedra centered at the origin and mid-edge is typically short (1.72 Å); this corresponds to the general observation (*1*) that interpolyhedral bonds are shorter than intrapolyhedral bonds in boron systems.

The triply condensed icosahedral B_{28} unit (which contains the B_{10} unit) girdles the equator of the B_{84} unit. In this unit, atoms B11 and B12 are shared between pairs of adjacent icosahedra and atom B14 is shared by all three. The coordination of B11 and B12 is eightfold while that of B14 is ninefold; all of the other atoms in the structure display sixfold coordination with one radial intericosahedral and five intraicosahedral bonds, except for B15 which is in a trigonal antiprism at the cell center.

The condensed icosahedra in the B_{28} unit display significant distortions from regularity. Most of the bond lengths range from 1.76–1.85 Å but B3–B3 is significantly longer at 1.90 Å and B4–B8 is significantly shorter at 1.725 Å; the over-all average of 1.81 Å is remarkably close to the usual value for intraicosahedral boron bonds.

The intericosahedral links joining the B_{28} unit into the equatorial belt of the B_{84} unit average 1.71 Å and the links to the central icosahedron are only 1.624 Å. Consequently, the B_{84} unit is markedly prolate with slightly large hexagonal openings at top and bottom.

In the B_{28} unit, atom B13 is located sufficiently close to the threefold axis that the B13–B13 distance is only 1.885 Å. This is close enough to represent a rather strong bond; the three-center bond in α-B_{12} is 2.025 Å. It appears from the analysis that an occupancy factor of two-thirds should be applied to this site. This suggests that only two of the three positions can be occupied in any unit cell. This conjecture is supported by the fact that the bond distance between B13 and the atom at the center of the cell, B15, is only 1.684 Å; it seems unlikely that a boron atom would form six short octahedral bonds to other boron atoms.

Finally, the B16 atoms are situated in the mirror planes of the cell within that truncated tetrahedral hole in the B_{84} unit which is intersected by the obverse rhombohedral cell faces. The interstitial atom appears to be located near the hexagonal face of the hole rather than at the centroid. The radius of the maximum insertable sphere is 1.115 boron radii (0.90 Å). The site occupancy factor derived from the least-squares and Fourier analyses was one-third of a boron atom. A detailed exploration of all other holes in the structure failed to reveal any major degree of occupancy.

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