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A Single-Crystal Diffractometry Investigation of Iron in β-Rhombohedral Boron

BENGT CALLMER AND TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

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The structure of a crystal of composition $FeB_{\sim 49}$ has been investigated using single-crystal diffractometry. The space group is $R\bar{3}m$ and the hexagonal cell dimensions are $a = 10.951$ Å and $c = 23.861$ Å. The three-dimensional boron network is essentially equivalent to that found in β-rhombohedral boron. Two sets of holes in this network are partially occupied by iron atoms.

Introduction

Determination of the structure of the solid solution of chromium in β-rhombohedral boron (*1*) has revealed that the chromium atoms partially occupy two sets of holes in the β-rhombohedral boron network and leave at least one set empty, which is large enough to accommodate chromium atoms. Similar solid solutions of the remaining 3*d* elements have been observed using X-ray powder data, and the cell expansion was measured and correlated with the microhardness (*2*, *3*). Recently, an investigation of the solubility of copper and manganese in β-rhombohedral boron (*4*) showed that atoms of these metals are distributed among three different sets of interstitial positions in the β-boron structure. It is evident that the different behavior of chromium, copper, and manganese in β-boron cannot be explained solely in terms of size factor restrictions, since copper and chromium have very closely equal atomic radii, so it seemed of interest to study how other transition metals atoms are distributed when dissolved in β-boron. Two Mössbauer studies of iron in β-boron have been reported, but even allowing for the difference in the sample preparation techniques used in the two investigations, the results obtained seem contradictory. In one of the investigations (*5*) it was concluded that iron, when dissolved in β-boron, occupies three different crystallographic positions. As a result of the other investigation (*6*) it was proposed that iron is substitutionally dissolved in β-boron. It was felt desirable to relate these results to a fundamental crystallographic study

Experiments and Crystal Data

Crystalline boron (Borax Consolidated, claimed purity 99.8 %) and iron rods (Johnson Matthey Chemicals Ltd., specpure) were arc-melted under an atmosphere of purified argon to a nominal composition corresponding to $FeB_{10.3}$. The crystal investigated was taken from this sample. The cell dimensions were measured for the single crystal as well as the solidified melt, using previously described techniques (*1*, *4*). From powder diffraction patterns it was established that the sample of nominal composition $FeB_{10.3}$ contained two phases, namely, FeB and a phase similar to the $CuB_{\sim 28}$ and $MnB_{\sim 23}$ phases previously reported (*4*). From the single-crystal refinement, the latter phase was found to have the composition $FeB_{\sim 49}$. The hexagonal cell dimensions of this phase were: from powder, $a = 10.9632(15)$ Å; $c = 23.867(4)$ Å; from single crystal, $a = 10.9514(8)$ Å; $c = 23.861(2)$ Å. The agreement between the two values for the *c*-axis is acceptable while the *a*-axis of the single crystal is slightly shorter than that of the powder, and the single crystal may thus contain less iron than the main part of the sample. However, the two cell dimensions measured are substantially larger than those of pure β-boron, which are $a = 10.9253(5)$ Å and $c = 23.8103(16)$ Å (*1*).

Intensities were recorded with an automatic STOE-Philips four-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation and the $\omega/2\theta$ scanning technique. The background was measured on each side of the scanning interval, which was 1.60°. All reflections up to $2\theta = 60°$ with $h \leq 0$, $k \geq 0$, and $l \geq 0$ were measured. The crystal had a maximum cross section of 0.12 mm and the calculated linear absorption coefficient for Mo$K\alpha$ radiation was 10 cm^{-1}. Weissenberg films were recorded to check the crystal quality and the symmetry.

The crystallographic calculations were performed using IBM 370/155 and IBM 1800 computers. A list of the programs used is given in (*4*). The atomic scattering factors, taken taken from (*7*), were corrected for anomalous dispersion according to Cromer (*8*).

Refinement of the Structure

The original set of data consisted of 1870 intensities, which were corrected for Lorentz and polarization effects. The $F_0{}^2$ values for equivalent reflections were averaged, after which the data were reduced to 919 independent structure factors, which included all observed reflections with $2\theta \leqslant 60°$ (Table I).

Using the coordinates and the temperature factors of the boron atoms in CrB$_{\sim 41}$(1), three-dimensional F_0 syntheses were calculated. In these syntheses peaks were found at the positions A(1) and D(1) (notation according to (*1*), the corresponding atoms are denoted Fe(1) and Fe(2) below). Approximate atomic coordinates and occupational parameters for the iron atoms were estimated from the F_0 and F_c syntheses. In the subsequent refinements the

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (× 10) FOR FeB$_{\sim 49}$

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
3	0	0	455	448
6	0	0	295	310
9	0	0	711	729
12	0	0	681	688
1	1	0	1061	985
4	1	0	482	516
7	1	0	364	358
10	1	0	475	461
2	2	0	150	152
5	2	0	104	104
•8	2	0	27	19
11	2	0	676	703
3	3	0	1705	1681
6	3	0	258	253
9	3	0	296	288
4	4	0	1696	1646
7	4	0	312	313
•10	4	0	79	66
5	5	0	1426	1409
8	5	0	684	686
6	6	0	2233	2236
•9	6	0	43	24
7	7	0	1008	988
•1	0	1	15	114
4	0	1	579	502
•7	0	1	89	90
10	0	1	863	848
•13	0	1	49	187
2	1	1	1404	1308
5	1	1	245	290
•8	1	1	87	129
11	1	1	333	360
0	2	1	486	495
3	2	1	458	426
6	2	1	119	104
9	2	1	295	242
12	2	1	357	375
1	3	1	489	434
4	3	1	708	732
7	3	1	604	595
10	3	1	627	396
2	4	1	679	662
5	4	1	102	79
8	4	1	240	209
0	5	1	679	667
3	5	1	711	750
6	5	1	192	188
9	5	1	248	218
1	6	1	922	970
4	6	1	339	309
7	6	1	181	213
2	7	1	118	70
5	7	1	278	271
8	7	1	424	402
0	8	1	844	900
•3	8	1	49	28
6	8	1	453	448
1	9	1	453	466
4	9	1	408	423
2	10	1	141	130
5	10	1	430	429
•0	11	1	91	37
3	11	1	118	101
1	12	1	182	201
2	0	2	448	445
5	0	2	117	80
•8	0	2	108	58
11	0	2	186	152
0	1	2	626	541
3	1	2	595	571
6	1	2	421	415
9	1	2	331	322
12	1	2	225	193
1	2	2	229	203
4	2	2	224	193
7	2	2	229	242
10	2	2	399	372
2	3	2	226	237
5	3	2	1030	1079
8	3	2	278	251
•11	3	2	130	153
0	4	2	1539	1425
3	4	2	104	131
•6	4	2	53	53
9	4	2	224	190
1	5	2	564	556
•4	5	2	65	51
7	5	2	285	260
•10	5	2	32	78
2	6	2	153	156
•5	6	2	98	138
8	6	2	271	253
0	7	2	152	204
•3	7	2	81	120
6	7	2	123	123
1	8	2	185	154
4	8	2	635	620
7	8	2	256	252
2	9	2	450	437
5	9	2	148	144
0	10	2	389	375
3	10	2	456	464
•1	11	2	84	90
2	12	2	189	237
•0	13	2	26	36
0	0	3	138	137
3	0	3	980	890
6	0	3	337	318
•9	0	3	123	159
•12	0	3	113	34
1	1	3	232	206
4	1	3	623	601
7	1	3	343	318
10	1	3	693	675
2	2	3	251	247
5	2	3	357	349
•8	2	3	84	25
11	2	3	775	750
0	3	3	472	467
3	3	3	1196	1186
•6	3	3	59	53
9	3	3	471	461
1	4	3	586	625
4	4	3	1330	1430
7	4	3	420	429
•10	4	3	171	24
2	5	3	253	247
5	5	3	968	962
8	5	3	276	261
0	6	3	2687	2706
3	6	3	414	420
6	6	3	283	287
9	6	3	433	427
1	7	3	1130	1207
4	7	3	266	262
•7	7	3	98	72
2	8	3	144	158
5	8	3	543	556
0	9	3	316	339
3	9	3	171	201
6	9	3	457	452
1	10	3	219	221
4	10	3	401	394
2	11	3	602	603
0	12	3	356	371
1	0	4	1676	1595
4	0	4	1880	1833
7	0	4	1187	1219
10	0	4	1087	1085
•13	0	4	183	55
2	1	4	345	317
5	1	4	1042	1038
•8	1	4	78	110
11	1	4	153	59
0	2	4	83	48
3	2	4	825	733
6	2	4	221	220
•9	2	4	98	92
•12	2	4	121	213
1	3	4	1539	1426
4	3	4	796	790
7	3	4	384	381
10	3	4	262	278
2	4	4	665	645
5	4	4	357	331
8	4	4	466	461
0	5	4	727	707
3	5	4	814	821
6	5	4	124	112
9	5	4	283	272
1	6	4	226	233
•4	6	4	93	82
7	6	4	940	907
2	7	4	846	825
5	7	4	805	773
8	7	4	484	507
0	8	4	130	22
3	8	4	598	590
6	8	4	258	222
1	9	4	775	773
4	9	4	214	206
•2	10	4	55	13
•0	11	4	82	45
3	11	4	359	321
1	12	4	952	963
2	0	5	444	411
5	0	5	1387	1352
8	0	5	834	877
11	0	5	427	448
0	1	5	316	356
•3	1	5	18	27
6	1	5	1153	1196
9	1	5	321	295
12	1	5	254	224
1	2	5	831	760
4	2	5	652	632
7	2	5	113	107
10	2	5	149	160
2	3	5	864	892
5	3	5	496	465
8	3	5	796	764
11	3	5	259	236
0	4	5	374	397
3	4	5	170	150
6	4	5	188	199
9	4	5	433	356
1	5	5	163	127
4	5	5	127	125
•7	5	5	81	63
2	6	5	356	351
5	6	5	573	586
8	6	5	676	655
0	7	5	1344	1385
3	7	5	247	243
6	7	5	139	113
1	8	5	303	317
4	8	5	340	341
7	8	5	334	339
2	9	5	364	367
5	9	5	332	337
0	10	5	777	829
3	10	5	145	133
1	11	5	1204	1217
•2	12	5	6	54
0	13	5	738	752
0	0	6	2323	2177
3	0	6	878	814
6	0	6	1366	1348
9	0	6	225	243
12	0	6	240	260
1	1	6	304	284
•4	1	6	77	77
7	1	6	611	616
10	1	6	140	191
•2	2	6	58	50
5	2	6	507	502
8	2	6	295	301
•11	2	6	33	112
0	3	6	900	851
•3	3	6	43	48
6	3	6	678	666
•9	3	6	109	77
1	4	6	576	605
4	4	6	432	423
•7	4	6	23	35
•10	4	6	84	84
2	5	6	537	546
5	5	6	609	625
8	5	6	370	365
0	6	6	692	726
3	6	6	312	308
6	6	6	127	159
9	6	6	276	237
1	7	6	289	309
4	7	6	741	743
7	7	6	120	121
•2	8	6	59	12
•5	8	6	103	75
•0	9	6	23	43
•3	9	6	84	54
6	9	6	187	169
1	10	6	128	136
4	10	6	141	153
2	11	6	375	376
0	12	6	1570	1577
1	0	7	430	411
4	0	7	823	871
7	0	7	512	591
10	0	7	690	697
13	0	7	469	429
2	1	7	225	148
5	1	7	704	684
•8	1	7	23	44
•11	1	7	98	145
0	2	7	1677	1609
3	2	7	99	36
6	2	7	633	643
9	2	7	549	583
•1	3	7	82	58
4	3	7	982	978
7	3	7	736	729
•10	3	7	29	29
2	4	7	585	584
5	4	7	407	392
8	4	7	236	236
•0	5	7	69	43
3	5	7	990	1012
•6	5	7	40	121
•9	5	7	67	78
1	6	7	473	478
4	6	7	335	317
7	6	7	698	702
2	7	7	245	243
5	7	7	168	119
8	7	7	247	265
0	8	7	401	383
3	8	7	465	452
6	8	7	608	617
1	9	7	583	558
4	9	7	127	133
2	10	7	250	244
0	11	7	1081	1064
3	11	7	393	413
•1	12	7	34	27
2	0	8	615	568
5	0	8	139	79
8	0	8	1157	1157
11	0	8	363	347
0	1	8	90	35
3	1	8	663	659
6	1	8	1362	1408
9	1	8	701	695
12	1	8	355	331
1	2	8	654	596
4	2	8	402	414
7	2	8	327	325
•10	2	8	89	130
2	3	8	2067	2018
5	3	8	292	268
8	3	8	213	198
11	3	8	909	936
0	4	8	256	307
3	4	8	1647	1689
6	4	8	584	596
9	4	8	399	392
1	5	8	95	69
4	5	8	546	541
7	5	8	700	718
•2	6	8	77	14
5	6	8	354	336
8	6	8	384	389
0	7	8	532	520
3	7	8	380	382
•6	7	8	23	64
1	8	8	791	794
•4	8	8	62	33
2	9	8	607	606
5	9	8	374	330
•0	10	8	24	9
3	10	8	873	879
1	11	8	577	591
0	0	9	1021	913
3	0	9	151	161
6	0	9	1040	1078
9	0	9	597	616
•12	0	9	41	84
1	1	9	493	456
4	1	9	157	85
7	1	9	103	107
10	1	9	875	843
2	2	9	262	251
5	2	9	145	133
8	2	9	197	199
•11	2	9	61	37
0	3	9	1267	1224
3	3	9	133	152
•6	3	9	76	115
9	3	9	374	375
1	4	9	316	332
4	4	9	449	481
7	4	9	498	512
10	4	9	262	257
2	5	9	715	749
5	5	9	267	278
8	5	9	342	331
0	6	9	424	437
3	6	9	364	333
•6	6	9	70	57
1	7	9	215	223
4	7	9	402	392
7	7	9	193	192
•2	8	9	96	29
•5	8	9	56	50
•0	9	9	87	110
3	9	9	258	276
•1	10	9	25	48
4	10	9	195	212
•2	11	9	26	67
0	12	9	587	565
1	0	10	251	207
4	0	10	1202	1212
7	0	10	382	345
10	0	10	1401	1375
2	1	10	445	436
5	1	10	616	607
8	1	10	351	337
11	1	10	580	566
0	2	10	1021	1071
3	2	10	91	59
6	2	10	234	242
9	2	10	266	269
1	3	10	795	751
4	3	10	399	457
7	3	10	703	690
10	3	10	353	342
2	4	10	1563	1592
5	4	10	100	32
8	4	10	726	721
0	5	10	148	143
3	5	10	519	544
6	5	10	351	355
9	5	10	439	448
•1	6	10	76	73
4	6	10	321	331
•7	6	10	26	23
•2	7	10	23	18
5	7	10	405	402
0	8	10	235	250
3	8	10	602	598
6	8	10	121	126
1	9	10	181	177
4	9	10	519	534
2	10	10	501	494
0	11	10	415	404
•1	12	10	88	63
2	0	11	775	757
5	0	11	615	665
8	0	11	334	346
11	0	11	762	755
0	1	11	1186	1152
3	1	11	1049	992
6	1	11	432	437
9	1	11	369	369
12	1	11	537	491
1	2	11	390	368
4	2	11	1021	1031
7	2	11	422	402
10	2	11	1187	1192
2	3	11	969	976
5	3	11	105	35
8	3	11	133	86
0	4	11	526	574
3	4	11	635	691
6	4	11	680	690
9	4	11	758	747
1	5	11	766	807
4	5	11	617	613
7	5	11	581	586
2	6	11	382	379
5	6	11	249	217
8	6	11	669	668
0	7	11	261	261
3	7	11	740	731
6	7	11	412	428
1	8	11	782	782
4	8	11	163	127
•2	9	11	24	29
5	9	11	214	214
0	10	11	224	235
3	10	11	716	727
•1	11	11	41	71
0	0	12	800	807
3	0	12	1037	1032
6	0	12	781	794
9	0	12	674	684
•12	0	12	39	124
1	1	12	360	360
4	1	12	305	323
7	1	12	178	192
10	1	12	318	327
2	2	12	543	503
5	2	12	330	313
8	2	12	587	584
11	2	12	388	373
0	3	12	1137	1110
3	3	12	1096	1111
6	3	12	356	346
•9	3	12	25	42
1	4	12	255	271
4	4	12	125	114
7	4	12	350	326
2	5	12	454	487
5	5	12	160	139
8	5	12	513	514
0	6	12	549	580
3	6	12	270	257
•6	6	12	25	41
1	7	12	141	121
4	7	12	254	238
7	7	12	176	179
2	8	12	913	897
5	8	12	389	385
0	9	12	476	487
3	9	12	213	155
•1	10	12	103	121
•2	11	12	39	19
0	12	12	222	134
1	0	13	674	650
4	0	13	1970	1968
7	0	13	348	352
10	0	13	1023	1001
2	1	13	112	112
5	1	13	377	403
8	1	13	303	323
11	1	13	426	412
0	2	13	1684	1655
•3	2	13	82	101
6	2	13	287	253
9	2	13	207	215
1	3	13	103	107
4	3	13	167	140
7	3	13	169	149
•10	3	13	103	114
2	4	13	1110	1154
5	4	13	322	323
8	4	13	429	401
0	5	13	508	458
3	5	13	690	662
•6	5	13	30	11
1	6	13	187	221
4	6	13	541	544
7	6	13	409	396
2	7	13	131	103
5	7	13	288	269
•0	8	13	59	35
3	8	13	597	593
6	8	13	873	867
1	9	13	142	154
4	9	13	138	147
2	10	13	294	292
0	11	13	181	163
•2	0	14	24	37
5	0	14	602	673
8	0	14	498	475
11	0	14	574	580
0	1	14	92	31
3	1	14	1258	1259
•6	1	14	69	108
9	1	14	296	312
•1	2	14	47	13
4	2	14	283	255
7	2	14	655	638
10	2	14	422	431
2	3	14	349	341
5	3	14	632	630
8	3	14	229	216
0	4	14	1101	1139
3	4	14	164	151
•6	4	14	79	79
9	4	14	521	524
•1	5	14	57	20
4	5	14	550	555
7	5	14	189	211
•2	6	14	66	78
5	6	14	704	677
0	7	14	694	691
3	7	14	480	461
•6	7	14	89	20
1	8	14	516	508
4	8	14	276	278
2	9	14	455	460
0	10	14	637	647
3	10	14	661	650
1	11	14	124	100
0	0	15	104	4
3	0	15	932	951
6	0	15	510	487
•9	0	15	29	19
1	1	15	651	645
4	1	15	216	231
•7	1	15	76	46
10	1	15	348	347
2	2	15	314	327
5	2	15	173	148
8	2	15	384	387
0	3	15	2161	2203
3	3	15	258	234
6	3	15	516	502
9	3	15	324	331
1	4	15	359	345
4	4	15	572	577
7	4	15	325	320
2	5	15	770	773
•5	5	15	24	61
6	5	15	493	494
0	6	15	288	262
3	6	15	1200	1203
6	6	15	308	289
1	7	15	132	107
4	7	15	467	480
2	8	15	172	168
5	8	15	897	888
0	9	15	226	236
3	9	15	288	295
•1	10	15	81	89
1	0	16	741	755
4	0	16	822	913
7	0	16	781	774
10	0	16	578	570
2	1	16	183	213
5	1	16	138	88
8	1	16	120	127
•11	1	16	28	28
0	2	16	1460	1453
3	2	16	232	236
•6	2	16	79	52
9	2	16	220	202
1	3	16	830	881
4	3	16	174	192
•7	3	16	91	56
2	4	16	705	697
5	4	16	299	275
8	4	16	152	137
0	5	16	132	75
3	5	16	336	338
6	5	16	420	403
1	6	16	484	498
4	6	16	1757	1721
7	6	16	467	473
2	7	16	312	307
5	7	16	747	724
0	8	16	575	560
•3	8	16	40	18
1	9	16	238	246
4	9	16	154	132
2	10	16	229	203
•0	11	16	26	15
2	0	17	596	592
5	0	17	765	749
8	0	17	327	326
11	0	17	447	477
0	1	17	546	538
3	1	17	435	445
6	1	17	386	389
9	1	17	156	125
1	2	17	1022	1077
4	2	17	502	488
7	2	17	778	752
10	2	17	244	248
2	3	17	160	137
5	3	17	308	311
8	3	17	195	249
0	4	17	331	350
3	4	17	257	268
•6	4	17	24	17
1	5	17	126	178
4	5	17	465	495
•7	5	17	26	33
•2	6	17	23	29
•5	6	17	84	93
0	7	17	289	287
3	7	17	1078	1037
6	7	17	538	501
•1	8	17	53	26
4	8	17	218	206
2	9	17	240	263
•0	10	17	25	12
0	0	18	179	188
3	0	18	502	500
6	0	18	976	952
9	0	18	192	196
1	1	18	521	549
4	1	18	655	657
7	1	18	188	223
10	1	18	400	396
2	2	18	318	313
5	2	18	228	222
8	2	18	777	794
0	3	18	669	736
•3	3	18	49	74
6	3	18	154	161
•9	3	18	119	180
1	4	18	119	132
4	4	18	638	585
•7	4	18	115	146
2	5	18	920	905
5	5	18	802	772
0	6	18	255	225
3	6	18	444	439
•6	6	18	27	56
1	7	18	551	550
4	7	18	1040	984
2	8	18	403	420
0	9	18	501	523
3	9	18	140	53
•1	10	18	112	35
1	0	19	952	1005
4	0	19	692	644
7	0	19	1021	1006
10	0	19	371	384
2	1	19	272	277
5	1	19	566	554
8	1	19	182	165
0	2	19	161	119
3	2	19	612	622
•6	2	19	91	112
•9	2	19	48	125
1	3	19	193	180
4	3	19	813	804
7	3	19	275	242
2	4	19	307	284
5	4	19	527	543
8	4	19	322	321
0	5	19	357	373
3	5	19	132	122
6	5	19	514	503
1	6	19	654	664
4	6	19	543	533
•2	7	19	25	55
5	7	19	153	123
0	8	19	845	849
3	8	19	162	106
1	9	19	254	268
2	0	20	462	461
5	0	20	649	685
8	0	20	547	584
0	1	20	160	85
3	1	20	120	123
6	1	20	472	445
•9	1	20	26	84
1	2	20	294	317
•4	2	20	34	66
7	2	20	173	154
2	3	20	244	235
5	3	20	354	336
8	3	20	273	248
0	4	20	142	167
3	4	20	432	421
6	4	20	170	120
1	5	20	472	478
4	5	20	111	144
7	5	20	217	174
2	6	20	195	192
5	6	20	666	666
0	7	20	777	782
3	7	20	621	647
1	8	20	237	222
4	8	20	806	822
2	9	20	214	196
0	10	20	221	193
0	0	21	539	560
3	0	21	145	176
6	0	21	244	259
9	0	21	165	163
1	1	21	390	403
4	1	21	815	788
7	1	21	885	880
2	2	21	217	205
5	2	21	461	459
8	2	21	601	605
0	3	21	813	817
3	3	21	257	243
6	3	21	554	547
1	4	21	144	121
4	4	21	225	217
7	4	21	127	35
2	5	21	199	186
5	5	21	304	296
•0	6	21	68	49
3	6	21	272	273
1	7	21	213	213
4	7	21	743	782
2	8	21	407	381
•0	9	21	26	19
1	0	22	632	650
4	0	22	213	212
7	0	22	1125	1095
10	0	22	808	792
2	1	22	612	672
5	1	22	251	263
8	1	22	427	444
•0	2	22	70	77
3	2	22	170	187
6	2	22	306	300
1	3	22	302	311
4	3	22	367	373
7	3	22	266	277
2	4	22	395	389
5	4	22	307	327
0	5	22	847	807
•3	5	22	50	53
6	5	22	1044	1006
1	6	22	362	369
4	6	22	381	388
2	7	22	362	352
0	8	22	246	225
3	8	22	647	654
1	9	22	283	273
2	0	23	153	113
5	0	23	874	853
8	0	23	755	758
0	1	23	370	353
•3	1	23	24	76
6	1	23	972	936
9	1	23	348	322
1	2	23	259	232
4	2	23	790	772
•7	2	23	26	68
2	3	23	478	464
5	3	23	211	207
0	4	23	1361	1400
3	4	23	376	392
6	4	23	158	121
1	5	23	228	241
4	5	23	280	230
2	6	23	122	94
•5	6	23	28	24
•0	7	23	24	40
3	7	23	360	397
1	8	23	389	381
0	0	24	150	116
3	0	24	644	641
6	0	24	422	433
•9	0	24	92	17
1	1	24	298	299
4	1	24	214	173
7	1	24	287	288
2	2	24	158	124
•5	2	24	80	79
8	2	24	201	196
0	3	24	536	507
•3	3	24	43	53
6	3	24	368	353
•1	4	24	24	8
4	4	24	508	495
2	5	24	173	170
•5	5	24	65	71
•0	6	24	91	13
3	6	24	185	192
•1	7	24	25	22
•2	8	24	70	8
•0	9	24	101	82
1	0	25	800	830
4	0	25	1119	1122
7	0	25	228	195
2	1	25	213	213
•5	1	25	109	130
8	1	25	190	151
0	2	25	142	138
3	2	25	329	335
6	2	25	815	800
•1	3	25	99	80
4	3	25	313	286
•2	4	25	62	72
5	4	25	193	201
0	5	25	1512	1440
•3	5	25	97	123
1	6	25	336	319
4	6	25	186	174
•2	7	25	100	44
0	8	25	934	945
2	0	26	787	778
5	0	26	366	357
8	0	26	1783	1747
0	1	26	598	615
3	1	26	292	284
6	1	26	412	401
1	2	26	591	599
4	2	26	178	188
7	2	26	299	293
2	3	26	547	529
5	3	26	316	299
0	4	26	1066	1052
3	4	26	344	349
1	5	26	398	417
4	5	26	270	265
•2	6	26	98	112
0	7	26	449	452
0	0	27	1118	1153
3	0	27	426	437
6	0	27	215	222
1	1	27	121	114
•4	1	27	71	98
7	1	27	280	240
•2	2	27	75	93
•5	2	27	100	51
0	3	27	1211	1202
3	3	27	235	232
1	4	27	400	386
4	4	27	409	411
•2	5	27	78	55
0	6	27	403	395
1	7	27	345	365
•1	0	28	54	73
4	0	28	465	461
•7	0	28	35	68
•2	1	28	102	89
5	1	28	268	271
0	2	28	119	55
3	2	28	201	179
6	2	28	269	238
•1	3	28	71	109
•4	3	28	103	118
•2	4	28	41	64
0	5	28	1441	1402
3	5	28	135	45
1	6	28	556	552
2	0	29	340	290
5	0	29	802	801
0	1	29	130	124
3	1	29	273	265
6	1	29	318	324
1	2	29	178	118
•4	2	29	79	73
2	3	29	122	34
0	4	29	1376	1396
3	4	29	264	249
1	5	29	504	440
•0	0	30	112	65
3	0	30	352	385
1	1	30	179	156
4	1	30	153	122
2	2	30	490	500
•0	3	30	52	46
3	3	30	913	912
1	4	30	233	241
1	0	31	200	173
4	0	31	212	189
2	1	31	372	394
0	2	31	155	133
3	2	31	222	257
1	3	31	879	863
0	5	31	429	426
•2	0	32	32	15
0	1	32	738	756
•3	1	32	95	4
•1	2	32	57	48
•0	0	33	31	37
1	1	33	169	200

least-squares program XTLALS (9) was used to refine one scale factor, the atomic coordinates, anisotropic, or isotropic temperature factors, and occupational parameters for the iron atoms and one boron atom. The function minimized was $\sum w(|F_0|^2 - |F_c|^2)^2$. Weights were used according to $w = 1/\{\sigma^2(F_0{}^2) + (C \cdot F_0{}^2)^2\}$ with $\sigma(F_0{}^2)$ obtained from counting statistics. The best weighting scheme was obtained with $C = 0.045$. The agreement index given below was defined as $R = \sum(|F_0| - |F_c|)/\sum|F_0|$.

Three different refinements were performed, namely, an anisotropic refinement using all 919 observed reflections, and an isotropic as well as an anisotropic refinement using a data set of 765 reflections (reflections with $\bar{F}_0{}^2 < 2\sigma(\bar{F}_0{}^2)$ were deleted and were marked with a dot in Table I). The type of refinement, the number of reflections used, and the *R*-values obtained were as follows: anisotropic, 765 reflections, 4.3%; isotropic, 765 reflections, 4.4%; anisotropic, 919 reflections, 5.4%.

The *R*-values obtained were lower for the smaller data set and the standard deviations of the atomic positions were somewhat larger, the increase being 6–9% for the anisotropic and 4–7% for the isotropic refinement as compared with the anisotropic refinement using 919 reflections. The atomic coordinates of the isotropic refinement using 765 reflections differed very little from those obtained in the anisotropic refinement of 919 reflections. The maximum difference was that found for the *y* coordinate of the partially occupied Fe(2) position. It was two-thirds of the standard deviation (0.0009 Å). The differences in the occupational parameters were also very small. The composition as calculated from the isotropic refinement (765 reflections) was $FeB_{48.81}$ and $FeB_{48.71}$ from the anisotropic one (919 reflections).

TABLE II

STRUCTURE DATA FOR $FeB_{\sim 49}$[a]

Atom	Position	*x*	*y*	*z*
B(1)	36(*i*)	0.17503(19)[b]	0.17544(19)	0.17689(7)
B(2)	36(*i*)	0.31875(19)	0.29492(19)	0.12892(7)
B(3)	36(*i*)	0.26155(19)	0.21724(19)	0.41965(7)
B(4)	36(*i*)	0.23580(18)	0.25150(19)	0.34683(7)
B(5)	18(*h*)	0.05465(13)	0.10930(13)	0.94412(10)
B(6)	18(*h*)	0.08596(13)	0.17192(13)	0.01329(10)
B(7)	18(*h*)	0.11048(14)	0.22095(14)	0.88704(10)
B(8)	18(*h*)	0.16968(14)	0.33936(14)	0.02790(10)
B(9)	18(*h*)	0.12900(14)	0.25801(14)	0.76628(10)
B(10)	18(*h*)	0.10226(14)	0.20451(14)	0.69834(10)
B(11)	18(*h*)	0.05651(13)	0.11301(13)	0.32662(10)
B(12)	18(*h*)	0.08991(14)	0.17983(14)	0.39848(10)
B(13)[c]	18(*h*)	0.05641(21)	0.11282(21)	0.55487(16)
B(14)	6(*c*)	0	0	0.38550(19)
B(15)	3(*b*)	0	0	1/2
Fe(1)[d]	6(*c*)	0	0	0.13528(4)
Fe(2)[e]	18(*h*)	0.20235(11)	0.40470(11)	0.17302(8)

[a] Space group $R\bar{3}m$ (no. 166). Hexagonal unit-cell dimensions: $a = 10.9514(8)$ Å, $c = 23.8609(16)$ Å. Cell volume: 2478.3 Å^3. (Rhombohedral unit cell: $a = 10.161$ Å, $\alpha = 65.22°$, $V = 826.1$ Å^3.)

[b] Standard deviations are given in parentheses and refer to the last decimal place of the respective values.

[c] Occupancy 72.6(11)%.

[d] Occupancy 50.7(3)%.

[e] Occupancy 18.5(2)%.

TABLE III

THERMAL PARAMETERS FOR $\mathrm{FeB}_{\sim 49}$ (IN Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
B(1)	0.517(63)[a]	0.538(65)	0.492(59)	0.300(52)	0.032(48)	0.033(48)	0.499
B(2)	0.361(60)	0.444(62)	0.383(57)	0.174(50)	−0.055(44)	−0.035(46)	0.408
B(3)	0.399(62)	0.510(64)	0.517(64)	0.266(52)	−0.030(46)	−0.042(45)	0.458
B(4)	0.364(61)	0.472(62)	0.403(59)	0.188(51)	−0.031(45)	−0.036(47)	0.423
B(5)	0.300(62)	0.300(62)	0.519(84)	0.143(71)	−0.002(33)	0.002(33)	0.376
B(6)	0.289(59)	0.289(59)	0.385(84)	0.101(69)	−0.001(33)	0.001(33)	0.340
B(7)	0.318(63)	0.318(63)	0.522(82)	0.101(71)	−0.062(33)	0.062(33)	0.412
B(8)	0.426(63)	0.426(63)	0.405(89)	0.193(71)	0.042(33)	−0.042(33)	0.428
B(9)	0.398(64)	0.398(64)	0.487(84)	0.195(73)	0.018(33)	−0.018(33)	0.430
B(10)	0.402(65)	0.402(65)	0.301(80)	0.212(72)	−0.024(32)	0.024(32)	0.363
B(11)	0.443(65)	0.443(65)	0.369(82)	0.277(74)	0.014(33)	−0.014(33)	0.394
B(12)	0.458(63)	0.458(63)	0.241(80)	0.228(72)	0.009(32)	−0.009(32)	0.386
B(13)	0.97 (12)	0.97 (12)	0.88 (15)	0.55 (12)	−0.046(53)	0.046(53)	0.912
B(14)	0.435(93)	0.435(93)	0.35 (14)	0.22 (5)	0	0	0.408
B(15)	0.79 (14)	0.79 (14)	0.09 (20)	0.392(72)	0	0	0.554
Fe(1)	0.257(31)	0.257(31)	0.210(41)	0.128(15)	0	0	0.241
Fe(2)	0.899(64)	0.899(64)	0.979(84)	0.397(63)	−0.031(28)	0.031(28)	0.950

[a] Standard deviations are given in parentheses and refer to the last decimal place of the respective values. B_{ij} is defined as $8\pi^2 U_{ij}$ where U_{ij} is the mean-square displacement tensor.

Evidently, the results of the three refinements differ very little. The decrease of the R value from 0.044 to 0.043, when anisotropic thermal parameters were introduced, is insignificant. Although the reduction of the data set from 919 to 765 reflections involves a decrease in the R value from 0.054 to 0.043, the standard deviations increase. We conclude that all 919 structure factors should be used in the refinement, since this gives the lowest standard deviations. The structure data, presented in Tables II and III, are based on 919 structure factors and anisotropic thermal parameters.

The two iron atoms, Fe(1) and Fe(2), were included in a final three-dimensional difference synthesis over the whole asymmetric unit. The largest deviation from zero for the electron density was 5 % of a boron maximum in the F_0 synthesis. Consequently, it was concluded that no further iron atoms are found in the structure.

Discussion

The crystal structure of β-rhombohedral boron was described and discussed in detail by Hoard et al. (*10*, *11*). Brief descriptions of the structure as well as the system of holes occurring in the structure were given later (*1*, *4*). Therefore, only a few remarks regarding the specific situation in $\mathrm{FeB}_{\sim 49}$ will be given below.

A comparison of the atomic coordinates of the boron atoms in pure β-boron with those in $\mathrm{FeB}_{\sim 49}$ reveals no great differences between the two structures. The three-dimensional boron network is essentially the same, and the largest deviation in boron–boron distance between the two structures occurs for the B(13)–B(14) distance, which is 0.032 Å shorter in $\mathrm{FeB}_{\sim 49}$.

The Fe(1) atoms are symmetrically surrounded by 12 boron nearest neighbors at a distance of 2.16 Å (Table IV), which is very close to the sum of the atomic radii of boron (0.88 Å) and of iron (1.27 Å). The Fe(1) atoms have no close metal neighbors. The Fe(2) atom have 14 boron neighbors at distances between 2.28 and 2.49 Å. The very short Fe(2)–B(13) distance (Table IV) is of rare occurrence, since occupancy of the two positions is low, namely, 19 % for Fe(2) and 73 %

TABLE IV

INTERATOMIC DISTANCES IN $\mathrm{FeB}_{\sim 49}$ (IN Å)

B(1)-B(9)	1.840(3)[a]	B(6)-B(8)	1.626(3)	B(13)-B(15)	1.691(4)
-B(2)	1.842(3)	-2B(6)	1.750(3)	-B(14)	1.780(5)
-B(2)	1.855(2)	-2B(5)	1.754(2)	-2B(3)	1.804(4)
-B(7)	1.856(3)	-B(5)	1.754(3)	-2B(13)	1.853(6)
-B(1)	1.912(4)			-2B(12)	1.862(3)
-B(1)	1.926(4)			-Fe(2)	2.033(4)
-Fe(1)	2.161(2)	B(7)-B(5)	1.725(3)	-2Fe(2)	2.449(3)
-Fe(2)	2.377(2)	-2B(2)	1.791(2)		
		-B(9)	1.809(3)		
		-2B(1)	1.856(3)	B(14)-3B(12)	1.733(2)
B(2)-B(3)	1.729(2)	-Fe(1)	2.162(2)	-3B(11)	1.767(4)
-B(7)	1.791(2)			-3B(13)	1.780(5)
-B(2)	1.822(3)				
-B(1)	1.842(3)	B(8)-B(6)	1.626(3)		
-B(9)	1.849(2)	-2B(4)	1.736(2)	B(15)-6B(13)	1.691(4)
-B(1)	1.855(2)	-2B(3)	1.797(3)	-6Fe(2)	2.484(2)
-Fe(2)	2.390(2)	-B(10)	1.838(3)		
-Fe(2)	2.419(2)				
		B(9)-B(10)	1.699(3)	Fe(1)-3B(5)	2.160(3)
B(3)-B(2)	1.729(2)	-B(7)	1.809(3)	-6B(1)	2.161(2)
-B(12)	1.785(2)	-2B(1)	1.840(3)	-3B(7)	2.162(2)
-B(8)	1.797(3)	-2B(2)	1.849(2)	-3Fe(2)	3.943(2)
-B(13)	1.804(4)				
-B(4)	1.829(2)	B(10)-B(9)	1.699(3)	Fe(2)-B(13)	2.033(4)
-B(3)	1.894(4)	-2B(11)	1.785(2)	-2B(3)	2.275(2)
-Fe(2)	2.275(2)	-B(8)	1.838(3)	-2B(1)	2.377(2)
-Fe(2)	2.470(2)	-2B(4)	1.841(2)	-2B(2)	2.390(2)
				-B(12)	2.401(3)
B(4)-B(4)	1.681(3)			-2B(2)	2.419(2)
-B(8)	1.736(2)	B(11)-B(14)	1.767(4)	-2B(13)	2.449(3)
-B(3)	1.829(2)	-2B(10)	1.785(2)	-2B(3)	2.470(2)
-B(10)	1.841(2)	-B(12)	1.828(3)	-B(15)	2.489(2)
-B(11)	1.847(2)	-2B(4)	1.847(2)	-2Fe(2)	2.503(2)
-B(12)	1.853(2)	-2B(11)	1.856(4)	-Fe(1)	3.443(2)
B(5)-B(7)	1.725(3)	B(12)-B(14)	1.733(2)		
-2B(6)	1.754(2)	-2B(3)	1.785(2)		
-B(6)	1.754(3)	-B(11)	1.828(3)		
-2B(5)	1.795(4)	-2B(4)	1.853(2)		
-Fe(1)	2.160(3)	-2B(13)	1.862(3)		
		-Fe(2)	2.401(3)		

[a] Standard deviations in parentheses. Distances listed at B-B <2.70 Å, Fe-B <3.0 Å, and Fe-Fe <4.0 Å.

for B(13). Full occupation of the Fe(2) positions would involve the formation of iron chains in the structure with iron-iron atoms distances of 2.50 Å. The structure determination of pure β-boron (*10*) revealed a partial occupation of the B(13) and B(16) positions. The occupancy of these positions as well as that of the metal positions have been collected in Table V for the solid solutions of chromium, manganese, copper, and iron in β-boron. It is evident from Table V that iron closely resembles chromium in its distribution

TABLE V

Partially Occupied Atomic Positions in Some β-Boron Structures

	Occupation (%)				
Atom	$CrB_{\sim 41}$ (*1*)	$MnB_{\sim 23}$ (*4*)	$CuB_{\sim 28}$ (*4*)	$FeB_{\sim 49}$	β-boron (*10*)
Me(1)	71.9(6)	25.6(7)	6.1(5)	50.7(3)	—
Me(2)	18.0(3)	43.1(5)	43.1(6)[a]	18.5(2)	—
Me(3)	0	66.2(8)	50.5(6)	0	—
B(13)	71.7(18)	65.0(23)	61.1(19)	72.6(11)	~67
B(16)	0	0	20.9(22)	0	~33

[a] The value refers to the sum of Cu(2′) in 18(*h*) and Cu(2″) in 36(*i*).

among the various sets of holes in the β-boron structure. The occupancy at the Me(1) positions is, however, lower for the iron atoms. Table V also shows that the occupation of the B(13) position is fairly independent of the introduced metal atom, while the occurrence of B(16) atoms seems to be coupled to a low occupation of the Me(1) position.

At the end of this investigation we became aware of a structure refinement of a crystal with the composition $FeB_{29.5}$ undertaken by Hughes and Tai at Cornell University (*12*). They found iron at the same atomic positions as we report here, although occupancy was higher at both positions due to the higher iron content of their crystal. Thus, it has been established in two independent investigations that iron dissolves interstitially in β-boron and that it is distributed between two different crystallographic positions. In view of this evidence it is impossible to accept the proposal by Stanke and Parak (*6*), based on a Mössbauer study, that iron is substitutionally accommodated in the β-boron structure.

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