tions at 0.4 and 25°. They estimate the accuracy of their determinations of the activity of water at about 1% above $m = 30$. Comparing their smooth table with the present results, Glueckauf and Kitt are lower by 1.3% at $m = 30$, 2.8% at $m = 40$, 1.3% at $m = 50$ and 3.6% at $m = 60$. They also give a result at $m = 70$ which is 7.3% low; however this appears to be extrapolated since the highest observation in a table of the actual observations kindly supplied to us by the authors was 66.73 molal. Aside from the 3.6% difference at $m = 60$, which occurs near the limit of the isopiestic method, the agreement is very satisfactory.

The Stability of the Low Temperature Phases in the H_2SO_4–H_2O System.—Ordinarily the temperature regions of stability of the various possible phases in a system are obtained by direct observation. This becomes increasingly impracticable due to decreasing rate of transition as temperature is lowered. In the present case data are available to obtain this information by calculation. One may inquire concerning such possibilities as

$$2H_2SO_4 \cdot 3H_2O = H_2SO_4 \cdot 4H_2O + H_2SO_4 \cdot 2H_2O$$

or

$$7H_2SO_4 \cdot 4H_2O = 2H_2SO_4 \cdot 6.5H_2O + 5H_2SO_4 \cdot 3H_2O$$

The free energy change in all such possible reactions was found to be positive at all temperatures down to 0°K. Thus no intermediate hydrate becomes unstable with respect to a higher and a lower hydrate. The calculations are straightforward and need not be discussed here. The possibility of a hydrate becoming unstable with respect to ice and a lower hydrate was also investigated. This case presents some calculation difficulties, since ice has residual entropy due to disordered hydrogen bonding at low temperatures; however, it is possible to conclude that none of the hydrates up to the hemihexa becomes unstable with respect to splitting out ice at low temperatures.

Acknowledgments.—We thank E. Glueckauf and G. P. Kitt for sending their detailed measurements and especially T. F. Young for exchanging data and coöperating in its interpretation.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY AND THE GENERAL ELECTRIC RESEARCH LABORATORY]

An Analysis of Polymorphism in Boron Based upon X-Ray Diffraction Results[1]

BY J. L. HOARD AND ARTHUR E. NEWKIRK

RECEIVED JUNE 29, 1959

X-Ray powder diffraction patterns are computed from single crystal data for tetragonal and β-rhombohedral boron. Critical examination of reported powder data from more than a dozen boron samples shows that (1) β-rhombohedral boron is generally to be expected from high temperature preparation with or without fusion, (2) besides the three established modifications, there are several other claimants to recognition. This multiplication of structural variants apparently is dictated by kinetic factors. It is suggested that boron prepared by deposition onto heated substrates is especially prone to form monotropes, often as non-stoichiometric borides.

Introduction

The definite characterization of three crystalline modifications of elemental boron has been in each case an immediate consequence of success in growing single crystals of these polymorphs.[2-4] More usually, the products obtained from boron-rich systems have been notably diverse microcrystalline aggregates, giving X-ray powder diffraction patterns which have defied simple interpretation. Such difficulties need no longer be exaggerated through lack of authoritative patterns for the established polymorphs. The powder diagram for (low temperature) *α-rhombohedral* boron has been published[5]; the patterns for *tetragonal*[2,6] boron and (high temperature) *β-rhombohedral*[3] boron, computed from spectrometrically measured single crystal data, are given in Tables I and II of this paper. When powder diffraction data from various preparations of boron, old and new, are examined in the light of the established patterns, the following general conclusions emerge.

The complex patterns have only too frequently been recorded at very low resolution on a heavy and rapidly varying background, to give spacings for low scattering angle sometimes not reliable to better than two significant figures. While use of accurate spacings from the single crystal data permits some allowance for apparently systematic trends in the reported values, the identification of phases achieved in these circumstances must be recognized as probable rather than certain. The advantages of recording with chromium Kα radiation, the longest generally practicable wave length, become so manifest that the line intensities of Tables I and II are given for this case.

Some powder diagrams from fairly pure boron samples indicate the existence of other polymorphs. We note specifically the recently obtained evidence for a second *tetragonal*[7] modification: namely, the successful indexing in terms of a very large cell (*ca.* 192 atoms) of some 50 lines from the diffractometer trace given by an apparently quite

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[1] Supported in part by a National Science Foundation Grant to Cornell University.

[2] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

[3] D. E. Sands and J. L. Hoard, *ibid.*, **79**, 5582 (1957).

[4] L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, *ibid.*, **80**, 2592 (1958).

[5] B. F. Decker and J. S. Kasper, *Acta Cryst.*, **12**, 503 (1959).

[6] J. L. Hoard, R. E. Hughes and D. E. Sands, THIS JOURNAL, **80**, 4507 (1958); *cf.* J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

[7] B. Post, private communication, 1959.

pure (*ca.* 99% B, little or no Al) microcrystalline preparation.[8] Although impressive, this evidence lacks the authority of single crystal data, and admits of no final appraisal at this time. However, it is useful to list, in order of decreasing intensity, the spacings of the seven most prominent powder lines[7] ($d \geq 2.82$ Å.) from this material: 5.03, 4.11, 4.30, 3.81, 3.36, 6.37, 3.93 Å., and to use this pattern in the later analysis quite as if it typified a fourth definite polymorph.

It probably is true that essentially pure boron can be prepared in an unusually large number of distinct crystalline patterns. Following consideration of the underlying reasons for this behavior, we shall suggest that most such "polymorphs" are monotropic forms which usually are more logically considered to be extreme cases of non-stoichiometric borides.

Powder Diffraction Patterns from Single Crystal Data.—The single crystal data employed for structure determination[6] of tetragonal boron yield the computed pattern of Table I. The lattice constants used, $a = 8.740$, $c = 5.068$ Å., from that single crystal presumed to have a minimum of structural defects, seem also to be fairly representative for the group of specimens studied. Recognizing, nonetheless, that the single crystal data do not preclude variations[6] in the lattice constants of the order of 0.5%, it has seemed wise to compute the powder diagram with a formal precision which can allow free exercise of individual judgment when interpreting a pattern recorded at high resolution. Of the 82 forms $\{hkl\}$ geometrically permitted with Cr Kα radiation, some 29 giving intensities substantially less than 1% of the maximum are omitted from Table I. The close approximation of the axial ratio, $a/c = 1.725$, to $\sqrt{3}$ means that distinct forms $\{hkl\}$ having a common value of the *approximate* quadratic form, $Q = h^2 + k^2 + 3l^2$, usually will not give resolved lines. For recording at low resolution with Cu Kα radiation, the spacings of the eight most prominent "lines" ($d > 1.30$ Å.), listed in approximate order of decreasing intensity will be: 4.37, 3.92, 2.43, 2.53, 1.44, 1.375, 2.19, 1.31 Å.

TABLE I

POWDER PATTERN FOR TETRAGONAL BORON FROM SINGLE CRYSTAL DATA

$a = 8.740$, $c = 5.068$ Å. Chromium Kα radiation.

hkl	*d*, Å.	*I*	*hkl*	*d*, Å.	*I*	*hkl*	*d*, Å.	*I*
110	6.180	3	113	1.630	6	361	1.262	5
011	4.384	9	142	1.626	2	162	1.250	9
200	4.370	100	151	1.624	1	550	1.236	3
111	3.919	75	123	1.551	1	024	1.217	3
121	3.095	11	251	1.546	2	053	1.215	2
130	2.764	2	440	1.545	6	262	1.213	9
002	2.534	24	600	1.457	5	071	1.212	5
031	2.526	10	133	1.441	29	460	1.212	7
131	2.426	75	342	1.439	18	124	1.205	2
022	2.192	2	152	1.420	1	153	1.203	3
231	2.187	19	260	1.382	16	452	1.202	2
330	2.060	1	161	1.382	13	224	1.172	3
141	1.956	6	252	1.367	21	253	1.170	1
240	1.954	2	143	1.321	3	271	1.168	1
331	1.908	9	451	1.318	20	362	1.159	30
132	1.868	1	333	1.306	13	134	1.152	3
042	1.655	2	004	1.267	8	370	1.148	6
051	1.653	5	062	1.263	1			

The powder diffraction pattern (Table II) for β-rhombohedral boron was computed from single crystal data taken by H. A. Weakliem and D. B. Sullenger at Cornell University using specimens from a macrocrystalline aggregate obtained in the Laboratory of the United States Borax & Chemical Corporation by crystallization from a melt ($\geq$ 99.4% B). The hexagonal lattice constants, $A = 10.944$, $C = 23.811$ Å., permit satisfactory *a priori* calculation of accurate settings for spectrometric intensity measurement of general $HK{\cdot}L$ reflections. The apparent thermal parameter is less than 0.5 Å.^{2}, and reflections of non-trivial intensity are measurable near the Mo Kα limit. The computational scheme of Table II is as follows:

TABLE II

POWDER PATTERN FOR β-RHOMBOHEDRAL BORON FROM SINGLE CRYSTAL DATA

$A = 10.944$, $C = 23.811$ Å. Chromium Kα radiation

HK·L	*d*, Å.	*I*	*HK·L*	*d*, Å.	*I*	*HK·L*	*d*, Å.	*I*
101[a]	8.806	<1	009	2.646	9	(2)	1.677	8
003	7.937	40	131	2.613	17	(2)	1.656	4
012	7.415	24	223	2.587	8	(2)	1.631	3
110	5.472	21	312	2.567	8	(2)	1.605	2
104	5.041	100	208	2.520	12	063	1.549	17
021	4.648	56	⎧306	2.472	10	606	1.468	9
113	4.505	28	⎨036	2.472	11	40·13	1.448	18
202	4.403	18	⎩217	2.467	8	(3)	1.430	28
015	4.255	25	134	2.405	17	(2)	1.418	22
006	3.969	17	119	2.382	9	164	1.405	4
024	3.708	23	401	2.360	11	(2)	1.382	30
211	3.542	28	042	2.324	13	440	1.369	6
122	3.430	17	10·10[a]	2.309	1	609	1.356	4
205[a]	3.359	2	315	2.301	2	(4)[c]	1.347	42
⎧116	3.213	1	128	2.289	3	15·11	1.338	9
⎩107	3.202	1	226	2.253	5	(2)	1.317	15
300[a]	3.159	<1	404	2.201	8	(5)[b]	1.302	25
214	3.074	6	321	2.165	2	11·18	1.286	10
⎧303	2.935	7	—	—	—	24·13	1.281	11
⎩033	2.935	1	137	2.080	4	(2)	1.259	11
125	2.863	19	(2)[b]	2.038	13	51·13	1.247	4
018	2.840	7	146	1.827	5	176	1.197	8
027	2.763	6	(2)	1.758	17	081	1.183	4
220	2.736	9	02·13	1.708	7			

[a] Unobserved on photograph described in text. [b] Slightly broadened. [c] Quite broadened.

All geometrically possible reflections for $d \geq 2.165$ Å. are included. The remainder of the table lists only those resolved "lines," often to some degree composite, which should be (and are) observable for $2.165 > d > 1.145$ A., when chromium Kα radiation is employed under conditions of reasonably good resolution and moderate exposure. Indices are listed wherever a single form is mostly or wholly responsible for the computed line intensity; otherwise (n) in the $HK{\cdot}L$ column is the number of forms giving substantial contributions to the intensity of the composite reflection of listed (weighted average) spacing.

Interpretation of Experimental Patterns.—Powder diffraction data for boron crystallized from high purity melts in two other laboratories are available for comparison with Table II. The pattern (from Dr. S. Geller) photographically recorded with Cr Kα radiation in a camera of $360/\pi$ mm. diameter from boron crystallized by

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(8) C. Talley, private communication to B. Post.

E. Corenzwit in the Bell Laboratories is very accurately described by the data of Table II, including details of line broadening for those few composite reflections where the effect is appreciable. Powder data (Cu Kα radiation) taken by Dr. F. H. Horn from boron purified by zone melting, and indexed with the aid only of computed spacings by L. E. Vogt and Dr. J. S. Kasper in the General Electric Research Laboratory, also are in generally very good, but of course less detailed agreement with calculation. It thus appears that the β-rhombohedral modification is reliably produced by crystallization from reasonably pure boron melts.

The powder pattern (Cu Kα) reported[2] for "needle" crystals and assumed to be authoritative for tetragonal boron, listed 16 prominent lines for $1.30 \lesssim d \lesssim 5.03$ Å., including (with satisfactory relative intensities) the eight expected to be most prominent and one other attributable to those three $\{hkl\}$ having $Q = 32$ (Table I). The remaining seven lines with spacings 5.03, 2.02, 3.33, 3.56, 2.70, 2.34, 1.74 Å., presumably characterize the microcrystalline matrix ensheathing the heated filament, from which sheath the tetragonal needles grew out along the thermal gradient; in taking "clusters of needles" for powdering a good deal of the substrate must have been included. None of these seven reflections is to be found among the stronger lines of the α-rhombohedral pattern. The spacing (5.03 Å.) of the strongest extra reflection is strikingly (but deceptively) similar not only to that of the forbidden $\{001\}$ of tetragonal boron but also to the spacings of the strongest lines (5.04 and 5.03 Å., respectively) in the patterns both of β-rhombohedral boron and of the Talley preparation mentioned in the Introduction. Noting, however, the absence from the listed extra reflections of the second, third and fourth strongest lines of the Talley sample, and of the 4.65, 7.94, 4.51 and 4.26 Å. lines of β-rhombohedral boron, we conclude that the microcrystalline sheath was largely some presently unidentifiable material able to contribute most or all of the 5.03 A. line intensity.

The experimental pattern showing the best agreement with the data of Table I is that of Mellor (Private Communication, 1938), taken from boron prepared by the same general method as used by Laubengayer,[2] *et al.* There is nearly quantitative agreement of relative intensities and spacings (within 0.01 Å. excepting $\{110\}$ and $\{111\}$) for eighteen lines with $d \gtrsim 1.21$ Å. The experimental pattern shows also six or seven lines incompatible with the tetragonal boron pattern, all very weak excepting one (3.47 Å.) estimated at 20% of the maximum. This spacing, from internal evidence probably accurate to 0.01 Å. does not correspond to a strong line in any established polymorph; moreover, the 5.03 Å. line of the earlier discussion is conspicuously absent from Mellor's data. The foreign material in Mellor's powder sample of tetragonal boron apparently was different in kind and smaller in amount than in the powder sample of Laubengayer, *et al.*

However, examination of the powder data reported earlier[9] by Mellor, *et al.*, leads to the following conclusions: (1) it is not certain that any established polymorph was present in the preparation, and (2) combinations of two or more of the known patterns do not carry the interpretation far enough to command confidence.

Interpretation of the powder data reported diagrammatically by Uno[10] for boron prepared by the general method of Laubengayer, *et al.*, is necessarily rather qualitative. Some of the purer (97–98% boron) materials prepared at 1150–1300° appear to have been largely tetragonal boron; the patterns as reproduced show no very strong extraneous lines. One sample, containing 6% Si and 6% Pb, gave a pattern much more strongly suggestive of β-rhombohedral boron, even though the temperature of preparation was given as only 1100°. There is further evidence (*vide infra*) that this highly complex structure can be formed at unexpectedly low temperatures provided an appropriate kinetic mechanism (probably involving initial solid solution or boride formation) becomes available.

Powder data from a dozen or more other preparations of boron remain to be discussed. It will simplify the presentation if we first take note of certain background material and state in advance a few general conclusions drawn from the analysis. (1) It is almost certain that β-rhombohedral boron is thermodynamically stable from the melting point down to 1500°, quite possibly to much lower temperatures. (α-Rh. $\rightarrow$ β-Rh. is directly observed[5] at 1500°.) The β-rhombohedral polymorph is identified as either a principal or the dominant phase in numerous preparations not involving fusion, occasionally at temperatures but little above 1000°. (2) The *possible* range of thermodynamic stability for tetragonal boron would appear to be something like 1100–1300°. There is no convincing published evidence to establish its presence in preparations other than those already discussed. (3) The consistency with which α-rhombohedral boron is obtained[5] by the pyrolytic decomposition of both boron triiodide and boron hydrides[11] on surfaces heated to 800–1100°, and its crystallization[12] from boron–platinum melts at 1200–800° delineate the approximate temperature range in which this is the expected and possibly the thermodynamically stable polymorph. Our examination of the powder diagram given by Robertson[13] in 1943 for boron prepared by reducing the bromide with hydrogen in a tube held at 750–800° identifies his material as being largely α-rhombohedral boron. However, this polymorph is at best doubtfully identified in but one other of the preparations now under scrutiny. (4) The Talley preparation (*Cf.* Introduction) resulted[8] from the pyrolytic decomposi-

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[9] D. P. Mellor, S. B. Cohen and E. B. Underwood, *J. Proc. Austral. Chem. Inst.*, **3**, 329 (1936).

[10] R. Uno, *J. Phys. Soc. Japan*, **13**, 667 (1958).

[11] W. L. Robb and L. C. Landauer, Abstracts of Papers, Boston Meeting of ACS, April, 1959, Division of Inorganic Chemistry, Paper 53.

[12] F. H. Horn, "Recent News," Electrochemical Society Meeting, Philadelphia, 1959.

[13] J. A. Robertson, Thesis, Cornell University Library, Ithaca, N. Y., 1943.

tion of boron tribromide on filaments (tungsten, molybdenums) which were heated to about 1250°. We find inconclusive evidence for its presence along with β-rhombohedral boron in one older preparation.

Cross comparison of the calculated patterns of Tables I and II shows that the certain identification of tetragonal boron in the presence of any considerable proportion of the β-rhombohedral phase demands reasonably quantitative treatment of both spacing and intensity data. The converse situation is less critical, *e.g.*, the identification of β-rhombohedral boron should follow readily from observation of the distinctive 5.04, 5.47, 7.415 and 7.94 Å. lines (provided these be recorded with some pretense to quantitative measurement). However, the "standard" pattern of Laubengayer, *et al.*, for tetragonal boron has been grossly misleading since (1) it included the very strong extra 5.03 Å. line virtually coincident with the strongest (5.04 Å.) line of β-rhombohedral boron, and (2) it listed only selected prominent lines; whoever recorded for his preparation the moderately intense 7.94, 7.415, 5.47 Å. lines while noting their absence from the "standard" listing would still have no means of evaluating their true significance. Given only cursory examination, the salient features of the "standard" pattern will seem to be reproduced rather satisfactorily by a powder photograph from β-rhombohedral boron whereas the absence of the intense 5.03 Å. line from a powder photograph of pure tetragonal boron will scarcely be overlooked. Thus those preparations of boron which have been reported to give powder patterns in agreement with that of Laubengayer, *et al.* (without specifying details) certainly were not pure tetragonal boron, more probably were largely or wholly the β-rhombohedral phase. In this category are the preparations by Fetterley[14] at 1400–1450° and by Johnston, *et al.*[15] at 1700°. Probably this latter preparation (at 1700°) was essentially pure β-rhombohedral boron, an important point since it was used for accurate heat capacity measurements.

Fourier integral analysis of the powder data from boron of better than 99% purity but unspecified preparative method indicates[16] ". . . . six nearest neighbors at an average distance of 1.89 Å. in crystalline boron." The eight prominent lines for 2.86 $\lesssim d \lesssim$ 7.99 Å. cited as characterizing this interesting material were taken from the microphotometer record of a powder pattern made with crystal monochromated Mo Kα radiation in a camera of 8.93 cm. diameter. Allowing for incomplete resolution (Mo Kα!) and some nearly systematic variations in matching spacings, the experimental pattern is essentially that expected from Table II for β-rhombohedral boron.

The pyrolytic decomposition of boron tribromide on heated tungsten or molybdenum surfaces gave[17] a "graphitic" deposit (apparently thus named solely on the basis of appearance) at 1000–1300°, and a "crystalline" sample at 1500–1600°. Powder data from the two preparations, 25 and 30 lines, respectively, were indexed in terms of 78-atom tetragonal and 180-atom hexagonal units. The indexing for "graphitic" boron is internally consistent, therefore possibly meaningful, but is in terms of a cell bearing little resemblance to that assigned by Post to the Talley preparation. With ostensible use of the same reaction and substrates at about the same temperature (1000–1300° as against 1250°), close similarity of products would seem normal. Although three pairs of strong reflections seem well-matched, the strongest (5.03 Å.) line of the Talley sample is not among the 25 reported for "graphitic" boron. (Lines of even larger spacing are reported[17] for the "crystalline" sample.) The four strongest lines of α-rhombohedral boron correlate with four strong lines of the "graphitic" pattern provided we accept consistently large (0.02–0.05 Å.) spacings for the latter. At least two "graphitic" lines of moderate intensity are geometrically incompatible with the Talley boron or with any established polymorph. Of course the unique but certainly very doubtful interpretation is to accept the "graphitic" preparation as a distinct polymorph.

Most of the lines reported[17] for the "crystalline" (1500–1600°) preparation are in fair agreement as regards spacings and intensities with the β-rhombohedral diagram. The reported 4.78 Å. (strong) and 5.23 Å. (weak) reflections, together with less than fully satisfactory correlation of some other lines with the data of Table II, require a significant admixture of some other presently unidentified material.

Among the more interesting microcrystalline samples of boron prepared by reducing boron tribromide with hydrogen on a hot tungsten filament was one for which the surface temperature during deposition ranged from 1550° at the beginning down to 1280° at the end of a run.[18] A powder photograph (Cu Kα radiation) of a fragment from the outer, more obviously crystalline layer, gave upwards of fifty lines for 1.11 $\lesssim d \lesssim$ 8.0 Å., but poor resolution and heavy background at low sin θ required spacings for $d \gtrsim$ 3.9 Å. to be rounded off to the nearest 0.1 Å. It seems necessary but not sufficient to assume that a large proportion of β-rhombohedral boron is present in the sample. The pattern expected with an admixture of the Talley boron, computed for the range $d \gtrsim$ 2.82 Å. in which data are at hand, is given in Table III. The unknown weight proportions correspond to assumed equal contributions from the strongest lines (5.03, 5.04 Å.) of the two materials. Table III has the merit of accounting very well for six of the seven strongest observed reflections. The worrisome discrepancies (6.37 *vs.* 6.6 Å., the predicted but unreported 3.36 Å. reflection) are for lines characteristic of the Talley preparation. The interpretation is suggestive but inconclusive.

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[14] G. H. Fetterley and W. M. Hazel, U.S.A.E.C. A2191. Declassified, Feb. 14, 1957.

[15] H. L. Johnston, H. N. Hersh and E. C. Kerr, THIS JOURNAL, **73**, 1112 (1951).

[16] T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950).

[17] St. v. Naray Szabo and C. W. Tobias, THIS JOURNAL, **71**, 1882 (1949).

[18] A. E. Newkirk, "The Preparation and Properties of Crystalline Boron," Thesis, Cornell University, Ithaca, N. Y., 1940.

Table III

Interpretation of Newkirk's Preparation as a Mixture

Spacing, Å.		Intensity		Spacing, Å.		Intensity	
Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
7.94	8.0	14	M	4.30	4.3	60	VS
7.42	7.5	8	VW	4.11	4.1	57	VS
6.37	6.6	20	M	3.94	3.9	23	W
5.47	5.6	7	VW	3.79	3.75	33	S
5.04	5.0	100	VVS	3.36	..	24	..
4.58	4.6	25	M	3.27	3.25	10	W
4.40	4.4	6	VW	2.89	2.91	10	W

Powder data have been reported[19] for three samples of boron prepared by the reduction of boron trichloride with hydrogen on titanium and graphite substrates at temperatures ranging from 1075–1200°. The 16 prominent lines given for the material deposited on titanium at 1100–1200° are, if allowance be made for use of Cu Kα radiation at comparatively low resolution, in excellent agreement with the requirements of Table II. If it be surprising to find β-rhombohedral boron formed directly at so low a temperature, it is then astonishing to find the material deposited on titanium at 1075–1125° giving a powder pattern (15 prominent lines) which is not interpretable in terms of any combination of the standard diagrams. Indeed the temperature ranges, curiously overlapping as cited, would formally indicate a sharp transition at or slightly below 1100°. Further, the material deposited on graphite in the 1075–1125° interval gives a powder diagram (12 prominent lines) quite dissimilar to that of the deposit on titanium for the same temperature range, of any of the previously discussed patterns, or of ordinary boron carbide. The substrate, whether titanium, graphite, tantalum, molybdenum or tungsten, was severely attacked. Stern and Lynds prefer titanium as substrate largely because[19] ". . . . it can readily be removed from boron by treatment with chlorine at temperatures (300–350°) well below the reported temperature (550°) for boron–chlorine combination." (It remains unclear whether the samples giving the cited diffraction data had received such treatment.)

Lagrenaudie[20] has reported powder diffraction data from eight well-crystallized boron samples, of which six (from Trombe) resulted from fusing amorphous boron, while the other two (from Hackspill) were prepared by decomposing boron tribromide (presumably in an arc or condensed spark discharge[21]). As noted by Lagrenaudie, the similarities of the eight patterns are far more striking than their differences, in general agreement with Cueilleron's statement[22] that the powder pattern of boron prepared by the Hackspill–Cueilleron method is similar to that obtained by fusing amorphous boron in the atomic hydrogen blowpipe. Comparison of the patterns with the data of Table II strongly indicates that every sample was largely the β-rhombohedral phase, but that none was wholly so. One of the Hackspill samples probably contained the largest admixture of another phase, a not unreasonable result in terms of the highly inhomogeneous thermal conditions implicit in the preparatory method. The (somewhat variable) inhomogeneity of the fused samples perhaps indicates incomplete fusion and recrystallization or, more probably, fractionation of impurities to give a small proportion of a second (boride) phase.

Lagrenaudie's interpretation of his powder data in terms of a mixture of boron polymorphs is a wholly unacceptable alternative. Apparently he set out to account for the composite pattern from all eight samples in terms of the known tetragonal form and one other, which he deduced to be also tetragonal. (A "superlattice" variant (with doubled c-axis) of the established tetragonal cell, designed to take care of at most two "extra" reflections from at most two samples, need not concern us.) As Lagrenaudie was necessarily misled by the listing of the very strong 5.03 Å. line in the "standard" tetragonal pattern of Laubengayer, *et al.*, he ended up with two polymorphs of which neither could account for the intense 5.04 Å. line appearing in all of his patterns. Most of the other lines attributed by him to the established tetragonal form are in better quantitative agreement with the β-rhombohedral pattern. The work cited earlier certainly makes β-rhombohedral boron the expected phase on crystallization from a pure melt at ordinary pressures. Simultaneous crystallization of *two* distinct polymorphs from the melt, implying the existence at low pressure of the least common type of triple point, seems truly improbable.

Powder data taken by Rollier[23] from boron supplied by Cueilleron are in evident disagreement with the latter's conclusion (cited above) as to the essential similarity of X-ray diffraction patterns from boron prepared by the condensed spark method and boron crystallized from the melt. Rollier's pattern is not interpretable in terms of any combination of the established diagrams. He was able to index the 21 observed lines in terms of a large hexagonal unit (a = 8.93, c = 9.8 Å., $Z \cong 90$ atoms) with a reasonable degree of internal consistency. This cell, of course, is not firmly established by so few data of limited resolution. In the absence of information as to the effective temperature and nature of the surface upon which this particular sample of boron was formed, any further discussion would be purely speculative.

Discussion

It can be said that published X-ray data have seemed, more or less convincingly, to support the existence of more than a dozen boron polymorphs. At one time or another no less than ten different elementary cells have been reported. Our analysis (*vide supra*) has apparently eliminated three of these: the two tetragonal cells of Lagrenaudie[20] (one of which was merely a "superlattice" version of the established tetragonal structure) and the hex-

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[19] D. R. Stern and L. Lynds, *J. Electrochem. Soc.*, **105**, 676 (1958).

[20] J. Lagrenaudie, *J. chim. phys.*, **50**, 629 (1953).

[21] *Cf.* L. Hackspill and J. Cueilleron, *Compt. rend.*, **218**, 458 (1944).

[22] J. Cueilleron, *Ann. Chim.*, **19**, 459 (1944).

[23] M. A. Rollier, *Proc. XIth Int. Cong. Pure Appl. Chem., London*, **5**, 935 (1947). Publ. 1953.

agonal cell of the "crystalline" boron of Naray-Szabo and Tobias.[17] Certainly eliminated is the tentatively suggested[2] pseudo-orthorhombic cell for plate-like single crystals in the preparation of Laubengayer, *et al.;* despite the curiously different habits, the needles and the plates (of hexagonal aspect) were shown[6] to have the same tetragonal structure. There remain, in addition to the established cells of α-rhombohedral, β-rhombohedral and tetragonal boron, three incompletely appraised cases: the (*ca.* 192 atoms) tetragonal cell of Post,[8] the (*ca.* 90 atoms) hexagonal cell of Rollier,[23] and the (*ca.* 78 atoms) tetragonal cell for the "graphitic" preparation of Naray Szabo and Tobias.[17] To this list of 3–6 possible polymorphs, we may need to add one or both of the 1075–1125° preparations of Stern and Lynds,[19] and, in time, possibly still others.

Before we accept the probability, much less the fact, of a virtually unbounded list of crystalline boron polymorphs, perhaps we should examine critically what we mean, or ought to mean by the term "polymorphic modification." It is in the first instance highly unlikely that a half dozen different modifications, each thermodynamically stable within a characteristic temperature interval, are to be crowded within the range, 1000–1500°. Insofar as we can judge, the very simple α-rhombohedral structure is the only crystalline form to be obtained below 1000°, while the extremely complex β-rhombohedral framework is reliably obtained above about 1500°. It is likely that the choice of framework below 1500° is dictated by kinetic rather than thermodynamic considerations, and that most of the polymorphs thus chosen are actually monotropes, *i.e.*, forms which are thermodynamically unstable with respect to transformation into the stable modification at every temperature. (We limit the discussion for obvious reasons to normally low pressures.) The occasional formation of the very complex β-rhombohedral phase at temperatures as low as 1100° is presumably the result of a favorable kinetic mechanism; the observed formation tends to support but does not certainly establish (*vide infra*) thermodynamic stability of β-rhombohedral boron at these lower temperatures.

It is our hypothesis that preparation of boron by deposition onto a heated and more or less severely attacked substrate is peculiarly likely to give rise to monotropes, some of which are properly to be classified as (limiting cases of) non-stoichiometric borides. It is probable that the structural pattern set during the initial stage of deposition and heavy attack upon the substrate must be appropriate to a phase, be it called boride or solid solution, which contains a fair proportion of substrate material (and other "impurities" if such be present). The born framework thus established, whether dictated by kinetic or thermodynamic considerations, need not invariably correspond to that of a pure boron polymorph stable at this or any other temperature. However, if the initially established framework be consistent with that of a stable modification of boron, continued deposition at a rate too rapid to be matched by the radial diffusion of substrate atoms should allow ultimate recovery of the essentially pure polymorph from the outer layers of the deposit; the formation of β-rhombohedral boron on titanium at 1100–1200° may well exemplify this simplest case. If the initially established framework be inconsistent with that of a stable modification of boron, continued deposition *without phase change* should ultimately yield pure crystalline boron as the non-stoichiometric boride or boron monotrope. However, if a new phase develops at a later stage of deposition, the new pattern could be that of a (still higher) boride, in which case the preceding analysis should apply, or that of a pure boron polymorph. The radial growth[2] of needle-like single crystals of pure tetragonal boron from a microcrystalline matrix of different structural pattern apparently belongs in this last category, but the matter deserves further comment.

Since the basic framework of the structure[6] contains holes (two/cell) large enough to accommodate tantalum or tungsten atoms, a stoichiometric boride, MB_{25}, is theoretically possible. The detailed structure analysis[6] placed an upper limit of 1/1400 on the atom fraction of tantalum in the tiny single crystal providing the diffraction data, but this figure would still permit filling of holes to the stoichiometric value for many layers during initial deposition. The real questions are: can an M/B ratio $\lesssim$ 1/25 but greater than some critical value actually dictate the choice of framework and, if so, was the M/B ratio in the matrix where single crystal nuclei were formed large enough to satisfy the critical condition? Although we surmise that the M/B ratio in the region of nucleation was so much less than 1/25 as to imply a perhaps improbably low value of the critical ratio for a non-stoichiometric boride mechanism to be operative, we cannot in fact answer the first question nor, *a fortiori*, the second. The distinction between mechanisms has possibly more theoretical interest than practical importance; the empirical evidence seems to suggest that for the temperature range in which tetragonal boron has been prepared it may be formed as a kinetically simpler but monotropic alternative to the β-rhombohedral polymorph.

That deposition (from $BCl_3 + H_2$) onto titanium and graphite at 1075–1125° gave materials[19] very different from one another and from the expected α-rhombohedral phase suggests that certainly one and probably both are properly classified as non-stoichiometric borides (or possibly mixtures thereof). That α-rhombohedral boron did not appear (in any detectable amount) at a later stage of deposition reinforces the impression that kinetic factors are controlling while casting some doubt on the claim of this polymorph to thermodynamic stability within the cited temperature range. Probably the α-rhombohedral structure is less able to accommodate foreign atoms in solid solution without disruption of framework than are the β-rhombohedral or tetragonal phases; the delta[4] bonds of the low temperature modification would seem to invite attack.

Our discussion seems to offer a rational basis to account for the otherwise bewildering array of structural variants displayed by reasonably pure boron preparations. It is noteworthy that this multiplication of structural variants seems practically to be concentrated within a temperature band (*ca.* 1000–1500°) below which the relatively very simple α-rhombohedral structure is consistently obtained, above which the highly complex β-rhombohedral framework is reliably produced. However, the integrated effect of the empirical observations is to suggest thermodynamic stability for the β-rhombohedral polymorph at all temperatures above approximately 1100°. The multiplication of structural variants and the only occasional production of the β-rhombohedral phase within the cited temperature band would then be attributable to restrictions on the growth kinetics.[24]

Acknowledgment.—We wish to express our appreciation to Dr. J. S. Kasper for his helpful comments.

[24] Readers of this paper may find useful two reviews, (1) Arthur E. Newkirk, "Preparation and Chemistry of Elementary Boron," and (2) J. L. Hoard, "Structure and Polymorphism in Elemental Boron," both to appear in the forthcoming volume "From Borax to Boranes" in "Advances in Chemistry Series," Amer. Chem. Soc., Washington, D. C. An extensive bibliography of publications dealing with elementary boron is given in (1).

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The Aromatic Reactivity of Ferrocene, Ruthenocene and Osmocene[1,2]

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Received June 15, 1959

Both ruthenocene and osmocene, like ferrocene, exhibit substitution reactions that are characteristic of aromatic systems. The electrophilic reactivity of these metallocenes decreases in the order: ferrocene > ruthenocene > osmocene. Ruthenocene undergoes hydrogen–metal interchange with n-butyllithium to a greater degree than does ferrocene. The gradation in reactivity of ferrocene, ruthenocene and osmocene, together with acid dissociation constant and infrared measurements, indicate a tighter ring-to-metal bonding in the higher molecular weight derivatives.

The discovery of ferrocene (I)[4,5] in 1951 has been followed by numerous chemical confirmations that the compound possesses an aromatic system.[6] In this respect, ferrocene undergoes Friedel–Crafts acylation[7] and alkylation,[8] can be formylated,[9] sulfonated,[10] metalated with n-butyllithium,[11,12] phenylsodium[13] and mercuric acetate,[11] arylated with diazonium salts,[11,14] and treated with isocyanates to produce N-substituted amides.[15,16] On the other hand, typical aromatic-type reactions such as nitration and direct halogenation lead to destruction of the molecule, presumably through oxidation of the iron atom.

Although cyclopentadienyl derivatives of most of the transition metals have now been prepared, no direct chemical evidence regarding the aromatic reactivity of these compounds (metallocenes) has yet been reported other than for ferrocene itself.[17] As already has been pointed out,[17c] many metallocenes may possess aromatic character and still not exhibit typical aromatic reactions as does ferrocene, because of the instability of the metallocene under the reaction conditions involved. Thus, attempts to prepare acyl derivatives of nickelocene under Friedel–Crafts conditions have been unsuccessful,[17c] and attempts to metalate cyclopentadienylmanganese tricarbonyl with n-butyllithium result in collapse of the molecule, even though Friedel–Crafts reactions are successful.[17a] The most logical metallocenes for investigations of the type described for ferrocene should be the dicyclopentadienyl derivatives of ruthenium(II)[18] and osmium(III),[19] since both compounds possess rare gas configurations and should be similar in chemical reactivity and stability to ferrocene. The results of these investigations are discussed below.

Ruthenocene (II) has been prepared previously in 20% yield by the reaction of ruthenium acetyl-

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[1] For a preliminary report of this work, see: M. D. Rausch, E. O. Fischer and H. Grubert, *Chemistry and Industry*, 756 (1958).

[2] The name "osmocene" is assigned for dicyclopentadienylosmium (II), in accordance with earlier suggestions of "ferrocene" for dicyclopentadienyliron(II) [R. B. Woodward, M. Rosenblum and M. C. Whiting, This Journal, **74**, 5531 (1952)], and "ruthenocene" for dicyclopentadienylruthenium(II) [G. Wilkinson, *ibid.*, **74**, 6146 (1952)].

[3] Monsanto Chemical Co., Dayton, Ohio.

[4] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[5] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

[6] For a review of the aromatic reactions of ferrocene, see: (a) P. Pauson, *Quart. Revs. (London)*, **9**, 409 (1955); (b) M. D. Rausch, M. Vogel and H. Rosenberg, *J. Chem. Educ.*, **34**, 268 (1957); (c) K. Schlögl, *Österr. Chem. Ztg.*, **59**, 93 (1958).

[7] R. B. Woodward, M. Rosenblum and M. C. Whiting, This Journal, **74**, 3458 (1952).

[8] A. N. Nesmeyanov and N. S. Kotschetkova, *Doklady Akad. Nauk S.S.S.R.*, **109**, 543 (1956).

[9] G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *Chemistry and Industry*, 209 (1957).

[10] V. Weinmayr, This Journal, **77**, 3009 (1955).

[11] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. S. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

[12] R. A. Benkeser, D. Goggin and G. Schroll, This Journal, **76**, 4025 (1954).

[13] A. N. Nesmeyanov, E. G. Perevalova and S. A. Beinoravitschute, *Doklady Akad. Nauk S.S.S.R.*, **112**, 439 (1957).

[14] G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[15] M. D. Rausch, P. Shaw, D. Mayo and A. M. Lovelace, *J. Org. Chem.*, **23**, 505 (1957).

[16] N. Weliky and E. S. Gould, This Journal, **79**, 2741 (1957).

[17] It has been reported recently by several groups of investigators [(a) E. O. Fischer, Division of Inorganic Chemistry, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958 (not in abstract); see also E. O. Fischer and K. Pletske, *Ber.*, **91**, 2719 (1958); (b) J. Kozikowski, R. E. Maginn and M. Klove, Division of Organic Chemistry, 134th Meeting of the American Chemical Society, Chicago, Ill., Sept. 7–12, 1958; see Abstracts of Papers, p. 58-P; (c) F. A. Cotton and J. R. Leto, *Chemistry and Industry*, 1368 (1958)] that cyclopentadienylmanganese tricarbonyl undergoes the Friedel–Crafts reaction.

[18] In contrast to the well established antiprismatic structure of ferrocene, the cyclopentadienyl rings of ruthenocene lie in an eclipsed configuration with respect to one another around the ruthenium atom (G. L. Hardgrove and D. H. Templeton, *Acta Cryst.*, **12**, 28 (1959)).

[19] Osmocene also probably possesses an eclipsed configuration (E. O. Fischer and H. Grubert, *Ber.*, *in press*)).