I THE STRUCTURES OF SOME COMPOUNDS OF BORON

II SOME OTHER STRUCTURAL STUDIES

Thesis by

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Acknowledgments

I would like to express my deepest thanks to Professor Linus Pauling, at whose suggestion I entered the field of molecular structure; to Professor Verner Schomaker who, as my Research Director, deserves the major credit for the work described in this thesis; to Dr. Kenneth Hedberg and Dr. Richard Marsh for their valuable help in solving many of the problems herein; to the Office of Naval Research and the Weirton Steel Company for their financial support; and finally to all of the staff members and graduate students with whom I have been associated for making my stay at the California Institute of Technology a pleasant one.

Abstract

Section I contains a description of the structural investigations of several compounds of boron, using electron diffraction and X-ray diffraction techniques. The structure of stable pentaborane has been determined and the interatomic distances and bond angles have been derived. The structure of tetraborane has been found and approximate values for the parameters are given. A possible model for unstable pentaborane has been found. A magnesium boride, MgB_2, has been prepared and shown to be isomorphous with AlB_2. A beryllium boride of approximate composition Be_2B has been prepared in impure form and shown to have a structure similar to CaF_2. An unsuccessful attempt has been made to prepare the copper boride Cu_3B_2 that is reported in the literature.

Section II contains a description of some other electron diffraction and X-ray diffraction investigations. The interatomic distances and bond angle in formyl fluoride have been determined. A partially successful study has been made of ozone. A reinvestigation of copper silicide has removed the major portion of an unpleasant random feature of the previous structure. A method has been devised for simplifying the calculation of theoretical intensity curves containing temperature factored terms.

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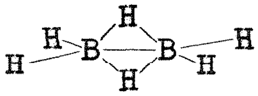
I THE STRUCTURES OF SOME COMPOUNDS OF BORON

Introduction

On the basis of early electron diffraction investigations, many of the boron hydrides were assigned molecular structures similar to those of the corresponding hydrocarbons. Diborane,(1) tetraborane,(2) unstable pentaborane,(2) and stable pentaborane(3) were described as being analogous to ethane, butane, pentane or isopentane, and methylcyclobutane respectively. The agreement between the observed and theoretical electron scattering curves for these configurations was, however, not as good as might have been expected even over the limited range of data: for example, a maximum in the scattering curve for stable pentaborane was predicted at a position where no maximum was actually observed. Moreover, these structures did not suggest any explanation of the relative stabilities of the various hydrides, in particular of the presumable instability of hydrides containing three boron atoms, none of which are known to exist.

More recent, spectroscopic investigations of diborane(4) verystrongly favored the bridge model,



A reinvestigation of diborane by electron diffraction was carried out by Hedberg and Schomaker(5). Careful comparisons of the observed scattering curves of ethane and diborane, especially in the difficult region of low <u>q</u> values, led to the same conclusion; that the bridge structure is the correct one.

Meanwhile, an X-ray diffraction investigation of the crystal structure of decaborane(6) had shown that this compound has a structure based on an icosahedron, with two of the icosahedron atoms removed, and also has bridge hydrogen atoms. It accordingly seemed likely that the bridge hydrogen bond might be an important factor in all of the boron hydrides and, since structures containing it were not studied in the early electron diffraction investigations of the two pentaboranes and tetraborane, reinvestigation of these compounds was evidently necessary. A reprint of a paper describing the successful investigation of stable pentaborane, and descriptions of the methods used to obtain the structure of tetraborane and a possible structure of unstable pentaborane are given in the following parts of this thesis.

At a point during the investigation of tetraborane, I noticed an interesting commentary on the original method for its preparation by the acid hydrolysis of magnesium boride. Stock remarks(7) that tetraborane seems to be a favored product of the hydrolysis, and suggests that the magnesium boride, actually a complex mixture, contains a compound Mg_6B_4 which is responsible for the formation of the hydrides. The interesting relationship of this boride, which might well contain B_4 units, to the structure of tetraborane led to a study of the preparation and crystal structure of magnesium boride. The totally unexpected results of this investigation created an interest in other metallic borides and led to studies of beryllium boride and copper boride. A detailed description of these investigations is given in the latter parts of this thesis.

Methods and Materials

Samples of stable pentaborane were kindly provided by Professor H. Schlesinger of the University of Chicago and by Dr. I. Shapiro of the Naval Ordnance Test Station in Pasadena. The samples of tetraborane and unstable pentaborane were prepared by Professor A. Burg and Mr. E. S. Kuljian of the University of Southern California. Immediately prior to the photographing, any hydrogen formed by thermal decomposition of the hydrides was removed by pumping at liquid nitrogen temperature. All other decomposition products have considerably lower vapor pressures than the primary compounds and would not interfere with the experiments.

Electron diffraction photographs of the three hydrides were prepared in the apparatus described by Brockway(8). The camera distance was 10.94 cm. for stable pentaborane and 10.985 cm. for tetraborane and unstable pentaborane. The electron wave length, 0.0608 Å for stable pentaborane and 0.0605 Å for the other two hydrides, was determined by zinc oxide calibration(9). For some of the photographs a beam catcher was used. Corrections were made in all cases for film expansion. The photographs of each compound were interpreted using the visual method.

Radial distribution curves were calculated(10,11) from the visual intensity curves according to the equation

$$rD(r) = \sum_{q=1,2,..}^{q\ max.} I(q)_{vis.} M(q) \sin \frac{\pi}{10} qr, \text{ where } q = 40/\lambda \sin$$

$\phi/2$, $I(q)_{\mathrm{vis.}}$ is the visually estimated intensity, and $M(q)$ is a modification function introduced in view of the fact that the data do not extend to an infinite scattering angle. In all cases radial distribution curves were calculated for $M(q) = \exp(-aq^2)$ with $\exp(-aq^2_{\mathrm{max.}}) = 0.1$. For both tetraborane and unstable pentaborane, curves were also calculated using $M(q) = Aq^4 \exp(-a'q^2)$ with A and a' adjusted to the conditions $Aq^4_{\mathrm{max.}} \exp(-a'q^2_{\mathrm{max.}}) = 0.1$ and $\int_0^\infty Aq^4 \exp(-a'q^2) = \int_0^\infty \exp(-aq^2)$, with $\exp(-aq^2_{\mathrm{max.}}) = 0.1$. Theoretical intensity curves were calculated(11,12) according to the equation(10) $I(q) = \sum_{i,j}{}' Z_i Z_j r_{ij}^{-1} \exp(-a_{ij}q^2) \sin \frac{\pi}{10} r_{ij} q$ using an effective Z value of 1.25 for hydrogen. The a_{ij} values used for diborane(5), 0.00016 for B-H$_{\mathrm{bond}}$, 0.00028 for B-H$_{\mathrm{bridge}}$, and 0.00062 for non-bonded B...H, were also used here in most cases.

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THE STRUCTURE OF STABLE PENTABORANE

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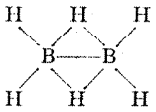
Stable pentaborane, B_5H_9, is one of the boron hydrides, a short, comparatively little studied series of extraordinary compounds for which a satisfactory elementary valence theory is lacking. In 1947 we decided to undertake new electron diffraction studies of the molecular structures. The early diffraction work and most of the theoretical discussion had been too much influenced (it now seems) by unfortunate analogies to ordinary valence compounds, and it had become reasonably clear that at least the old, ethane-like structure for diborane was incorrect and that a bridge structure (I) was more likely. In the case of B_5H_9, also, the structure from the previous diffraction study[1] was not in complete agreement with the appearance of the photographs, one of which was available to us. The bridge structure of diborane has now been well established,[2] the crystal structure of decaborane ($B_{10}H_{14}$) has been determined,[3] and the B_5H_9 structure has been determined, both from the gas diffraction pattern in the work here to be described[4] and from an x-ray study of the crystal by Dulmage and Lipscomb.[5] The most impressive attempt at a theory of the compositions and structures, however—Pitzer's protonated double bond theory,[6] which based the structures of all the boron hydrides on diborane bridges and on some plausibly assumed conjugation properties of these bridges—has been a casualty: each of the new boron hydride structures has shown little over-all relation to the previous ones and neither involves the diborane bridge.

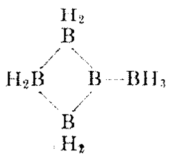


(I)

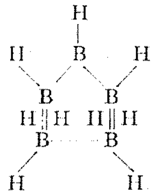
The Structure Determination.—The method used has been outlined in recent reports from this laboratory.[7]

New photographs were taken with samples kindly provided by Professor H. I. Schlesinger of the University of Chicago and by Doctor I. Shapiro of the Naval Ordnance Test Station, Pasadena. The camera distance was 10.94 cm. and the electron wave-length 0.0608 Å. Independent visual interpretations of the photographs were made by two observers (see Fig. 1).

The radial distribution curves, showing only two strong peaks, at 1.74 Å. (B—B) and 2.57 Å. (B···B and B···H), exclude both the structure advocated in the original study[1] (II) and that proposed by Pitzer[6] (III):



(II)



(III)

II would requre significant B···B interactions at $1.74 \sqrt{2} = 2.46$ Å. and at $2 \times 1.74 \sin 135°/2 = 3.22$ Å., at least if it were normally rigid, and III at an average of $2 \times 1.74 \sin 108°/2 = 2.82$ Å. (The original specification of III would also require the 1.74 Å. peak to be obviously doubled.) The radial distribution curves did not lead directly to the structure, mainly because neither the relative areas of the widely separated main peaks nor the indicated absence of minor interactions outside them could be relied upon.

Nevertheless, the radial distribution information provided a starting point for a more detailed analysis of the visual curves themselves. This analysis first showed that the observed doubled character of maximum 9–10 requires two groups of B—B interactions, of about equal weight, separated by 0.11 ± 0.01 Å. Even then, the outer part of the observed intensity curve, including max. 9–10, could not be reproduced without severely restricting the distribution of weights and distances within the 2.57 Å. radial distribution peak, either by making the distribution essentially continuous (corresponding to severe "temperature" factors) or in other ways which, given the B—B split, were fairly obvious. Finally, when this was done on the assumption that the 2.57 Å. peak was due mainly to rigid B···B interactions, it appeared that the B—H terms were probably also split, by about 0.15 Å. into two groups of about equal weight. Corresponding to this distance information three unsymmetrical arrangements of the boron atoms, a puckered five-membered ring, a dimethylcyclopropane-like arrangement, and an ethylcyclopropane-like arrangement, all actually rather closely similar, were found.

Before constructing and testing actual models based on these arrangements of boron atoms (the theoretical intensity curves already calculated lacked the B···H terms), we decided to re-examine the tetragonal pyramid arrangement, which had been considered but rejected in the original diffraction study, had more recently been further advocated by Pauling,[8] and, unlike our unsymmetrical arrangements, was in agreement with recent indications of high symmetry from spectroscopic[9] and calorimetric[10] data. The 2.57 Å. peak now had to be attributed mainly to B···H rather than B···B interactions, contrary to our previous assumption,[11] but with the help of the previous analysis a suitable disposition of hydrogen atoms was readily found (Fig. 2) and all others of full symmetry (C_{4v}) were ten-

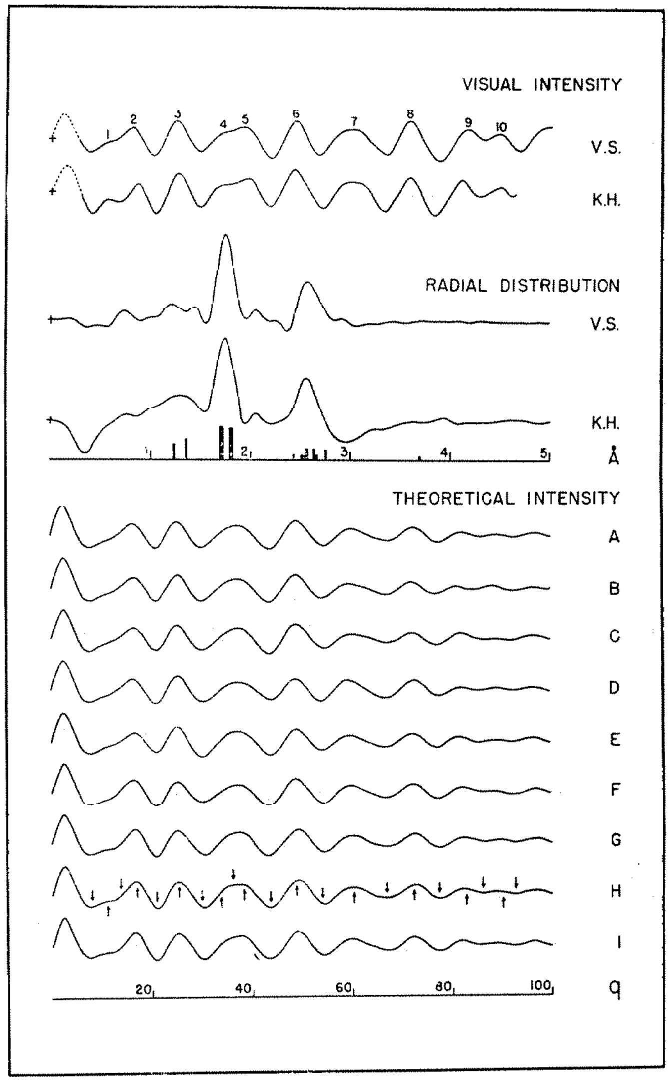


FIGURE 1.

Electron diffraction curves. The theoretical intensity curves are for the following pyramidal models:

CURVES	B—Hav./B—Bav.	B—B split	B—H split	$< B_1B_2B_2$	external dihedra $< B_1B_2B_2\text{-}B_2B_2H_3$
A	1.275/1.740	0.100	0.150	90°	180°
B	1.275/1.745	0.110	0.150	90°	180°
C	1.275/1.740	0.100	0.050	90°	180°
D	1.275/1.710	0.100	0.250	90°	180°
E	1.225/1.740	0.100	0.150	90°	180°
F	1.325/1.740	0.100	0.150	90°	180°
G	1.275/1.740	0.100	0.150	115°	180°
H	1.275/1.740	0.100	0.150	115°	190°
I	1.275/1.740	0.100	0.150	125°	190°

tatively eliminated. The new structure, with the B_2—B_2 and B_2—H_3 distances the longer of their respective kinds, seemed plausible and met with immediate success.

All except H · · · H terms were included for the theoretical intensity curves. The coefficients a_{ij} of the temperature factors $\exp(-a_{ij}q^2)$ were taken as 0.00016 for B_2—H_2 and B_1—H_1, 0.00028 for B_2—H_3, 0.00060 for B · · · H, and zero otherwise, as for diborane,[2b] and the effective value 1.25 was used for Z_H Of the selection of curves shown in Fig. 1, *G*, *H*, and *I* are acceptable, *A*, *B*, and *C* are doubtful, and *D*, *E*, and *F* are unacceptable. Important items for these conclusions are the depth of min. 4, the shape of doublet 4-5, the relative intensities of minima 6, 7, 8, and 9, the shape of max. 7–min. 8, and the position and shape of doublet 9-10. For the best curves, the only point of substantial disagreement concerns the heights of the first three main maxima; it is almost inconsequential for the parameter determination and probably arises from an underestimate, such as could be expected, of the height of the broad inner max. 1-2.

In terms of B—$B_{av.}$ = 1.740 Å. the best shape parameter values and estimated limits of error, together with the ranges for which intensity curves were calculated, are: B—$H_{av.}$, 1.288 ± 0.044 Å. (1.22–1.35 Å.); B—H_{split}, 0.125±0.090 Å. (0.05–0.35 Å.); B—B_{split}, 0.105 ± 0.010 Å. (0.09–0.12 Å.); ∠ B_1—B_2—H_2, 120 ± 20° (85–125°); and external dihedral angle $B_1B_2B_2$-$B_2B_2H_3$, 187 ± 10° (165–200°), all for the assumed C_{4v} symmetry. These values and the values of $\langle q_{calc.}/q_{obs.}\rangle_{av.}$ (see table 1 for an example) lead to the following results for the bond lengths: B_1—B_2, 1.700 ± 0.017 Å.; B_2—B_2, 1.805 ± 0.014 Å.; B_1—H_1 and B_2—H_2, 1.234 ± 0.066 Å. (B_1—H_1 = B_2—H_2 assumed); and B_2—H_3, 1.359 ± 0.077 Å.

The limits of error are conservative except that no allowance has been made for the possible effects on the angle determinations of our rough assumption that the previous guess for $a_{B \cdots H}$ in diborane should apply to B_5H_9, for all the different B · · · H terms. The concentration of all the B · · · H distances within the 2.57 Å. peak makes the question of interaction between temperature factor and distance parameters more serious than usual, but the boron parameters and probably the B—H distances should not be much affected, since they are determined largely by the outer part of the pattern, where the B · · · H contribution is in any case small. It may be noted that the crystal[5] and gas values for the bond angles and bond lengths in B_5H_9 are in good agreement except for the B—B lengths, for which the crystal values (1.66 ± 0.02 Å. and 1.77 ± 0.02 Å.) are shorter than ours by possibly significant amounts compared to the limits of error. Our B—B lengths, however, are in good agreement with the preliminary results 1.69 Å. and 1.80 Å. of a recent microwave investigation,[12] from which none of the other parameter values have yet been reported.

The x-ray confirmation of the structure type, which was communicated to us during our parameter determination, made unnecessary any further study of other possibilities, including the unsymmetrical ones described above. The high over-all symmetry and especially the C_{4v} skeletal symmetry have also been confirmed by the microwave investigation.[12]

Discussion.—The B_5H_9 structure has high ligancies, two for the bridge hydrogen atoms, five for the apical boron atom, and six for the basal boron atoms, in agreement with the principle[13] that electron deficiency gives rise to structures showing ligancies in excess of the respective numbers of suitable atomic orbitals. For the count of ligands, we take the direct B—B interaction of a bridge bond as bonding, although the related B···B interaction in diborane is often regarded as not bonding. We believe our assumption is the more likely one in view of the comparatively short B—B distance. It also makes the ligancies of hydrogen and boron in the boron hydrides and other high-ligancy compounds of boron more uniformly consistent with the high-ligancy principle, and is the natural assumption to make if these compounds are to be related to ordinary covalent compounds in terms of resonance, following Pauling's discussion of the metals.[14] Pauling's relation $r_n = r_1 - 0.300 \log_{10} n$ yields an attractive correlation of the actually very widely varying bond distances,[15] as well as inferences about certain other aspects of the structures. For example, the boron radius which would be exactly compatible with the bond distances of our preliminary report for B_5H_9 is 0.795 Å., in excellent agreement with the average 0.794 Å. obtained from all these compounds.

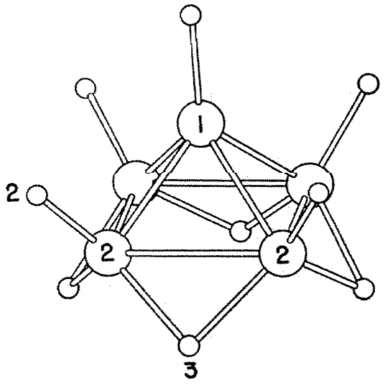


FIGURE 2.
The B_5H_9 structure.

The basal boron atoms of B_5H_9 and the apical boron atoms of $B_{10}H_{14}$ form just the same set of bonds; similarly, the apical boron atoms of B_5H_9 resemble the boron atoms of the calcium boride structure in an octahedron arrangement except for replacement of external B by H. As King and Lipscomb pointed out,[16] moreover, the whole B_5H_9 structure is related to the calcium boride structure in almost precisely the same way as the $B_{10}H_{14}$ structure is related to the boron carbide structure.[17] We may add that the basal boron atoms of B_5H_9 and all the boron atoms of decaborane, as well as the boron atoms of boron carbide and the icosahedron atoms of elementary boron (in the modification of known structure[18]), all have six ligands in the icosahedron arrangement, with bond angles approximating the ideal values of 60°, 108°, and $121\frac{3}{4}$° about as well as would seem possible under the constraints imposed by differing bond lengths and incompatible over-all symmetries.[19] Accordingly, it seems reasonable to suggest that these structures all reflect a strong tendency for sexiligated boron to adopt approximately the ideal icosahedron arrangement.

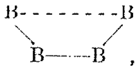
The occurrence of the icosahedron and octahedron arrangements is remarkable because they are notably anisotropic, in violation of what might be expected to result from the sp^2 (and sp^3, for the hydrides) hybrid orbitals on which the bonding is presumably mainly based and because there is surely no lack of more conventional alternatives. For elementary boron, for example, ordinary octahedral coordination in the simple cubic structure would seem suitable, especially in view of its frequent occurrence in complex structures for other atoms which are regarded as forming six half-bonds.[20] To be sure, the icosahedron and octahedron arrangements would seem less anisotropic if the external bonds were stronger than the internal bonds, as indeed is the general indication for B_5H_9 and decaborane. For the basal boron atoms of B_5H_9, for example, the bridge B—H, bridge B—B, and slant B—B bonds have the respective Pauling bond numbers 0.46, 0.45, and 0.67, with a total of 2.49, or only about three times the bond number 0.77 of the B—H external bond.[15] But for boron carbide, elementary boron, and calcium boride there is no definite indication one way or the other. Altogether, a proper understanding of the details of the bonding is lacking.

TABLE 1

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS OF MAXIMA AND MINIMA FOR MODEL H

	$q_{obs.}$				$q_{calc.}/q_{obs.}$			
	V. S.		K. H.		V. S.		K. H.	
NO.	MAX.	MIN.	MAX.	MIN.	MAX.	MIN.	MAX.	MIN.
1	11.19	7.76	10.89	8.06	(0.956)	(0.979)	(0.983)	(0.943)
2	16.41	13.31	17.31	13.88	(1.012)	(0.939)	(0.959)	(0.901)
3	25.00	20.47	25.34	21.03	1.012	1.021	0.998	0.994
4	33.87	29.70	33.33	29.77	(1.025)	1.024	(1.041)	1.021
5	38.52	35.41	39.66	36.42	(0.971)	(1.011)	(0.943)	(0.983)
6	48.70	43.46	48.59	43.62	1.008	0.999	1.011	0.995
7	59.51	53.53	60.45	54.25	1.000	1.014	0.991	1.007
8	72.66	66.95	71.87	66.61	0.998	1.004	1.009	1.009
9	83.29	78.03	82.23	76.50	(0.984)	0.993	(0.997)	1.013
10	90.07	86.50	89.97	85.57	(0.989)	0.991	(0.991)	1.002
11	..	93.23	..	91.89	...	0.992	...	1.007
			Average, 12 features		1.0047		1.0048	
			Average deviation		0.009		0.007	

Nevertheless, it seems unlikely that the immediate bond arrangement in these structures is superior. Instead, the essential point may be that they allow an increase in ligancy without a corresponding increase (or even with a decrease) in the number and severity of close non-bond interactions: compare, for example, the joined icosahedron unit of the boron and boron carbide structures with the simple cubic structure. In the latter, each atom has twelve next-nearest neighbors related to it by 90° bond angles, whereas the icosahedron atom has only five internal next-nearest neighbors at 108° and five external next-nearest neighbors at 122°. This strongly suggests that the next-nearest interactions are repulsive and important and that the high-ligancy principle should be revised to say that the high ligancies tend to be achieved in such a way as to minimize the numbers and maximize the distances of next-nearest neighbors, even if the resulting bond arrangements would appear by standards of ordinary covalence to be unduly strained. It may also account for the lack of apparent extra strength of the external bonds where two octahedra or two icosahedra are joined: for the icosahedron, again, each external bond would be opposed principally by ten next-nearest interactions at 122° and ten second-nearest interactions (assuming the staggered orientation of groups about the external bond) of the type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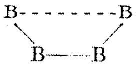
whereas each internal bond is opposed (a full counting shows) by only one internal next-nearest interaction at 108°, two external next-nearest interactions at 122°, and one external interaction of the type



in the opposed orientation. The present situation is evidently related to the cases of cyclopropane and cyclobutane,[21] where the energy and C—C bond length in cyclobutane are both greater than normal, apparently because of cross-ring repulsion, while in cyclopropane, in which the repulsion is avoided by formation of the three-membered ring, the bond length is less than normal and the energy still greater than normal, both apparently in consequence of the angle strain. In the high-ligancy boron compounds the relationships are no doubt different, especially because of the complicated resonance situation; nevertheless, the importance of next-nearest neighbor repulsions seems to be verified and there is the additional indication that angle-strain shortening of the internal bonds may also occur. For the calcium boride structure, of course, the role of the metal atoms has also to be considered.

We should like to express our thanks to Professor Pauling for his continued helpful interest in the investigation.

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[2] (*a*) Price, W. C., *J. Chem. Phys.*, **16**, 894 (1948): **15**, 614 (1947). (*b*) See also Hedberg, K., and Schomaker, V., *J. Am. Chem. Soc.*, **73**, 1482 (1951).

[3] Kasper, J. S., Lucht, C. M., and Harker, D., *Acta Cryst.*, **3**, 436 (1950).

[4] Hedberg, K., Jones, M. E., and Schomaker, V., *J. Am. Chem. Soc.*, **73**, 3538 (1951).

[5] Dulmage, W. J., and Lipscomb, W. N., *Ibid.*, **73**, 3539 (1951).

[6] Pitzer, K. S., *Ibid.*, **67**, 1126 (1945).

[7] See Hedberg, K., and Stosick, A. J., *Ibid.*, **74**, 954 (1952).

[8] Private communication.

[9] Pitzer, K. S., and Pimentel, G. C., private communication.

[10] Taylor, W. J., Beckett, C. W., Tung, J. Y., Holden, R. B., and Johnston, H. L., *Phys. Rev.*, **79**, 234 (1950).

[11] We had at first rejected the tetragonal pyramid (see reference 4), mainly because its relative number of $B\cdots B$ interactions and relative $B\cdots B$ distance ($1.74\sqrt{2} = 2.46$ Å.) are in disagreement with this false interpretation of the 2.57 Å. peak and because, in view of this interpretation, little attention was given to the (crucial) disposition of the hydrogen atoms. Our initial failure to recognize the B—B split also contributed to the argument on the apparent B—B—B angle (i.e., the ratio 2.57/1.74). Actually, the half-width of the 1.74 Å. peak is somewhat greater than would be expected from our convergence factor for zero split (although less than for a 0.10 Å. split). We overlooked this, failing to consider how little widening would result from distance splits up to 0.10 Å., especially in the absence of a well-resolved, sharp term to make the slow decline of the split-term contribution obvious in the appearance of the photographs. (In reference 13 the radial distribution distances were misquoted as 1.76 Å. and 2.62 Å.; also, in the discussion of the puckered five-membered ring model, it was not made clear that for the theoretical curve mentioned the hydrogen terms were neither based on an actual model nor complete. The complete curve was no longer promising; the original curve, lacking the B—B split, of course never was a good fit to the outer part of the pattern.)

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[16] Private communication; see references 4 and 5.

[17] Clark, H. K., and Hoard, J. L., *J. Am. Chem. Soc.*, **65**, 2115 (1943); Zhdanov, G. S., and Sevast'yanov, N. G., *Compt. rend. acad. sci. U. S. S. R.*, **32**, 432 (1941).

[18] Hoard, J. L., Geller, S., and Hughes, R. E., *J. Am. Chem. Soc.*, **73**, 1892 (1951).

[19] Our values for B_5H_9 are $\angle B_1B_2B_2 = 58^\circ$, $\angle B_2B_2H_3 = 48\frac{1}{2}^\circ$, and $\angle H_3B_2H_3 = 113^\circ$; $\angle B_1B_2H_3 = 106^\circ$, $\angle B_2B_2H_3 = 113^\circ$, and $B_2B_2B_2 = 90^\circ$; and $\angle H_2B_2B_1 = 120^\circ$, $\angle H_2B_2B_2 = 134^\circ$, and $\angle H_2B_2H_3 = 108^\circ$. Here the four-membered ring, the differences of B—H (bridge) and B—B bond lengths, and the evident need for large $\angle H_3B_2H_3$ to provide a reasonably long $H_3\cdots H_3$ distance, which we presume to be non-bonding, are obviously serious constraints; nevertheless, the average external angle is 121°, in surprising agreement with the ideal value. Also, our value 120° for $\angle B_1B_2H_2$ approximately equalizes the external angles, and the smaller, crystal value of 115°, which by the quoted ±5° limit of error is considerably more reliable than ours, equalizes the apparent strains very well indeed.

[20] Rundle, R. E., *J. Am. Chem. Soc.*, **69**, 1327 (1947).

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Tetraborane: B_4H_{10}

A careful examination of the photographs by K. Hedberg and M. Jones led to the visual intensity curve and corresponding radial distribution curve shown in figure 3. The strong radial distribution peak at 1.855 Å was assigned to bonded B-B interactions. This peak has a half width of 0.098 Å, slightly greater than the value of 0.090 Å expected for a single distance; it is therefore compatible with such a single distance, or with two or more distances split by as much as 0.1 Å. The radial distribution peaks in the region 1.26-1.54 Å were assigned to bonded B-H interactions which are obviously split into two or more groups. The indication of distances in the neighborhood of 1.40 Å seems to confirm the presence of bridge hydrogen atoms in the molecule, since in the known hydride structures these bridge distances are about 1.35-1.40 Å whereas the normal B-H bonds are about 1.20 Å. The 1.54 Å peak does not correspond to any expected distance and may be due to errors in the visual intensity. The 0.83 Å peak is surely caused by errors in interpretation. The broad and asymmetric peak at 2.65-2.85 Å was assigned a distribution of both B...B and B...H non-bonded interactions, as in the case of B_5H_9; it is hopelessly unresolved. The $Aq^4 \exp(-aq^2)$ radial distribution curve does, however, seem to yield some further information about the distribution of terms under the peak. This curve gives greater emphasis to data at larger values of q than does the normal $\exp(-aq^2)$

function, and might therefore be expected to cause peaks due to the relatively highly temperature factored B...H terms to decrease appreciably in size relative to peaks due to the more rigid B...B terms. (The theoretical $Aq^4 \exp(-aq^2)$ peak shapes of Fig. 3 show this effect.) A careful comparison of the two radial distribution curves indeed shows that the inner portion of the peak decreases noticeably in size relative to the outer portion, indicating that if any B...B interactions are present in the molecule they probably lie under the outer portion of the peak at a distance of about 2.85 Å.

The task of thoroughly studying the scattering intensity from all of the many possible configurations generally compatible with the radial distribution curves and containing four boron atoms and ten hydrogen atoms, and of investigating a sufficiently large range of parameter variations for each possible configuration to determine the likelihood of obtaining a fit to the data, is truly a monumental one. It was therefore decided to use an aspect of the radial distribution curves which is ordinarily less reliable than its indications of distance values; namely, the relative peak areas.*

The tetraborane molecule has six boron to boron interactions of which from three to six may be bonds,

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*The relative areas of the B-B and non-bonded B...B-B...H peaks proved to be reliable in the case of stable pentaborane. The area of the bonded B-H peak was not in good agreement, and for that reason the corresponding peak for tetraborane was not used in the following argument.

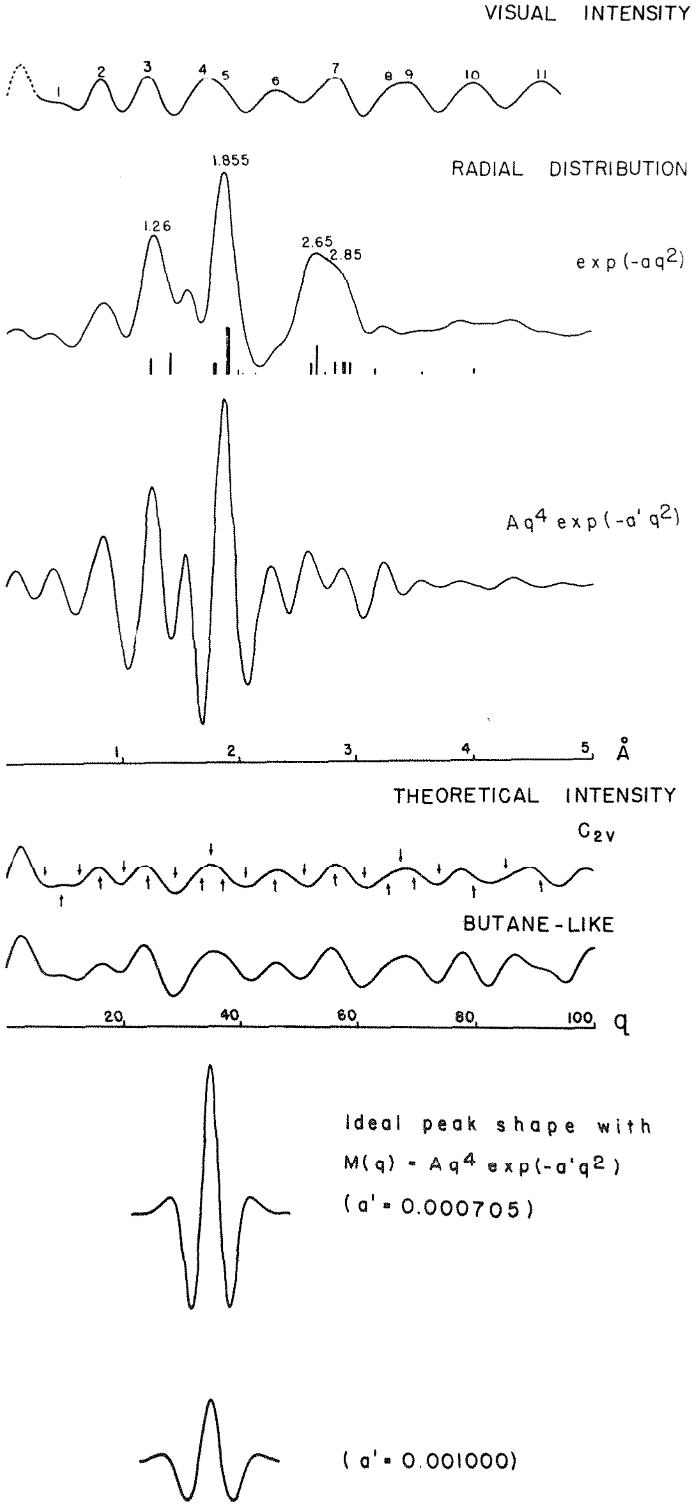

Fig. 3. Tetraborane curves

and the remainder non-bonds. Aside from the 2.65-2.85 Å peak, only the 3.85-4.30 Å peak lies at a great enough distance and has sufficient evident area to contain a non-bonded boron-boron interaction. And since the only plausible configuration with a B...B distance as long as 3.85 Å is a B_4 chain, we may assume that for all other configurations the non-bonded B...B terms either all fall in the region 2.65-2.85 Å or have, some of them, extremely severe temperature factors, a possibility which we ignore for the present. It is then possible to calculate, for any assumednumber of boron-boron bonds, the number of B...H interactions, in addition to the remaining number of B...B interactions, which must lie in the 2.65-2.85 Å region in order to fit the observed peak areas. The results of this calculation are shown in Table 2.

Table 2

no. B-B	no. B...B at 2.65-2.85 A	no. B...H at 2.65-2.85 A
6	0	30
5	1	21
4	2	12
3	3	3
3 (chain)	2	7

Now the total number of boron-hydrogen interactions is forty, of which ten or (if bridge bonds are present) more are B-H bonds. Since the radial distribution curve appears to show that bridge bonds are present, it seems reasonable to assume that there are about fourteen B-H bonds, leaving about twenty six long interactions to be disposed of. Since it is improbable that all of these could be made to fall in the 2.65-2.85 Å region*, or that as many as nineteen, or even fourteen, would fall outside it without being noticeable elsewhere on the radial distribution curve, five and four become the most likely numbers of B-B bonds, with five the most likely. The relative area of the 1.27 Å peak indicates twelve and nine B-H bonds respectively. It must be realized, of course, that these conclusions are not necessarily valid; we have merely shown that the five bond models will be capable of giving the best agreement with the radial distribution peak areas and therefore have, in this respect, the best possibility of yielding a good fit to the data.

For each boron configuration that was considered, reasonable hydrogen distributions were assumed, the parameters were adjusted in order to obtain approximate agreement with the radial distribution curve, and a theoretical intensity curve was calculated. In most cases only a rather superficial study was made of the probable effects on the calculated curves of varying the parameters for each configuration, but a much more

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*Twenty four out of the thirty four B...H interactions in B_5H_9 fell under the corresponding radial distribution peak.

thorough study was made in the case of the butane-like model reported by Bauer from his electron diffraction investigation(2), and in the case of models containing four or five boron-boron bonds as suggested by the analysis of the radial distribution curve.

Several theoretical intensity curves were calculated for butane-like models. The model reported by Bauer is in disagreement with the radial distribution curves, since the tetrahedral B-B-B bond angle leads to a strong peak at 3.03 Å. The curve for a model with a bond angle of 90° is fairly satisfactory (Fig. 3). However, no attempt was made at the time to carry out a complete parameter determination and, in view of developments which will be described later, no further work was done on the butane-like model at all.

Models containing four boron-boron bonds could not be made, it seemed, to give a good fit, but models containing five boron-boron bonds showed immediate promise and excellent curves were readily obtained. This C_{2v} model (Fig. 4), in addition to being in agreement with the data, was extremely pleasing, especially in comparison with the known structures of the other boron hydrides, and for this reason was believed to represent the actual structure of tetraborane, a belief which was born out somewhat later by a low-temperature X-ray investigation of crystalline B_4H_{10} by Nordman and Lipscomb.(13)

Once the correct molecular configuration of tetraborane has been established, a determination of accurate parameter values is desired. The C_{2v} B_4H_{10} structure is particularly unfortunate, however, because a total of twelve parameters, in addition to temperature factors, have to be fixed, because all of these are of roughly the same importance, because only two of them can be eliminated on the basis of reasonably safe assumptions, and because, in spite of the implication of detail, the pattern is actually very simple. The non-bonded distances to hydrogen atoms may often be assumed, since both individually and collectively they have little effect on the total scattering curve. However, the relatively large number of non-bonded boron-hydrogen distances in tetraborane, the relatively high value of Z_H/Z_B, and the fact that the majority of these distances are nearly alike, make it essential here to include them among the parameters to be adjusted to the data.

It is virtually impossible to use the correlation procedure for a problem of this complexity, since a minimum of about 3^n curves are required for solving an n parameter problem. The possibility of carrying out a least squares refinement of the parameters was therefore considered, and a preliminary refinement was made; however, the results were not satisfactory and it was finally decided that the data were simply not adequate (in number and quality) to precisely fix all ten parameters, or even

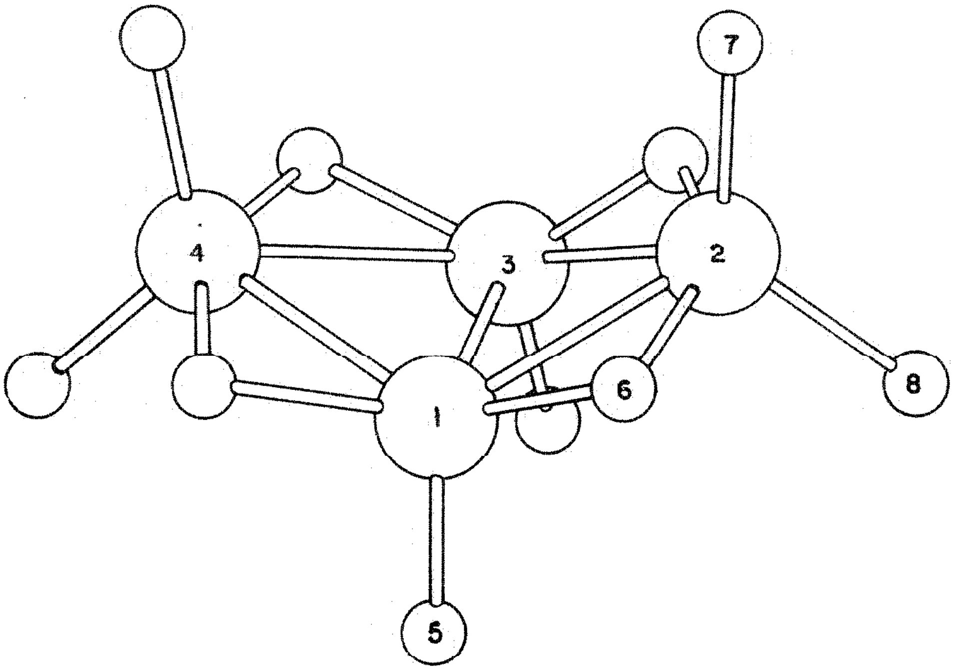

Fig. 4. C_{2v} structure of tetraborane.

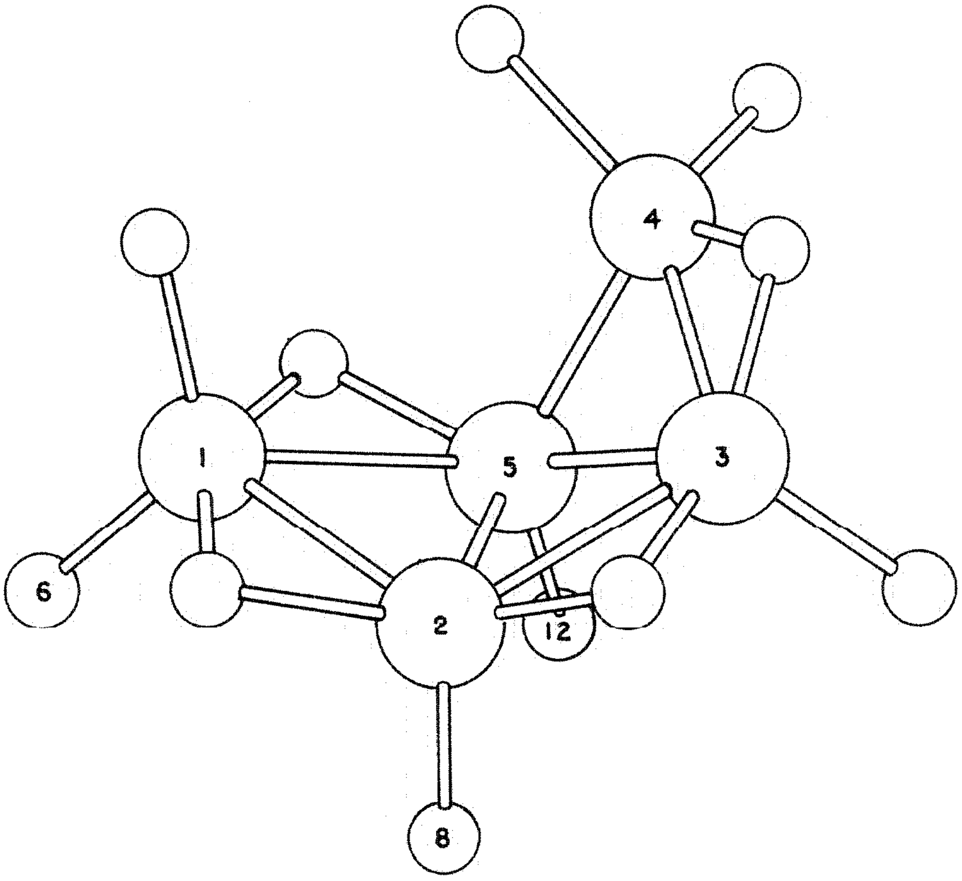

Fig. 5. Possible model of unstable pentaborane.

any interesting combination of them. The following method was used to obtain a set of parameters which is certainly near to the correct one. A theoretical intensity curve which was in good agreement with the data was chosen and the contribution of each individual parameter was determined. The effect of each parameter on that particular feature of the curve which needed the greatest improvement was noted, a decision was made as to which variations would best improve the feature without causing major changes of the remainder of the curve, and a new theoretical curve was calculated. This procedure was repeated until it was felt that no further substantial improvements could be made. The resulting parameter values, giving the curve shown in Figure 3, are B_1-B_2 = 1.87 Å, B_1-B_3 = 1.78 Å, B_2-B_4 = 2.92 Å, B_1-H_5 = B_2-H_7, B_2-H_8 = 1.21 Å, B_1-H_6 = 1.45 Å, B_2-H_6 = 1.35 Å, $B_4 \ldots H_5$ = 2.76 Å, $B_1 \ldots H_7$ = $B_1 \ldots H_8$ = 2.65 Å, and $B_4 \ldots H_6$ = 2.96 Å.*

Application of the scale factor (table 3) to these parameters yields the following interatomic distances: B_1-B_2 = 1.85 Å, B_1-B_3 = 1.76 Å, B_2-B_4 = 2.88 Å, B_1-H_5 = B_2-H_7 = B_2-H_8 = 1.19 Å, B_2-H_6 = 1.33 Å, and B_1-H_6 = 1.43 Å. The direction of the split in the bridge hydrogen distance is most uncertain since changing its sign has no noticeable effect on the curves, and even the existence of the

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*For this model, a value $a_{B\text{-}H}$ = 0.00040 was used for the bridge hydrogen atoms.

split itself is questionable. It is mainly a consequence of the low amplitude of maximum 6, and in view of a reexamination of the original photographs, together with those of a new sample of tetraborane,* this amplitude is in considerable doubt. Moreover, it was concluded from a consideration of the boron atoms involved in the bridge bond that a split in the bridge hydrogen distances would not be expected. Each boron forms two bridge bonds and one bond to hydrogen; the central boron forms a half bond to another boron, while the apical boron forms a three-quarter bond to hydrogen. If the resulting charge on the hydrogen atom is then neutralized by transfer of one-quarter of an electron from the apical boron, the bridge bond would be symmetric.

The parameters obtained by Nordman and Lipscomb from their X-ray investigation of tetraborane(13) are B_1-B_2 = 1.845 Å, B_1-B_3 = 1.750 Å, B_2-B_4 = 2.786 Å, B-H_{bond} = 1.11 Å, B_1-H_6 = 1.21 Å, and B_2-H_6 = 1.37 Å. The bonded B-B distances are in excellent agreement with our electron diffraction results, but the B-H bond distance is

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*An examination of the photographs by Professor Schomaker showed that those of the new sample were different in some respects from the older ones. In particular, the amplitude of maximum 6 appeared to be much closer to the average of maxima 5 and 7, and minima 6 and 7 appeared to be more nearly equal. The new photographs also appeared to die out more rapidly at high scattering angles. His conclusions based on the old photographs alone were in excellent agreement with our earlier interpretations, even to the extent of differing in just such a way as to account for the 0.83 Å error peak in the radial distribution curve.

Table 3

min.	max.	$q_{calc.}$	$q_{obs.}$	$q_{calc}/q_{obs.}$
1		7.4	(6.50)	(1.138)
	1	9.6	(9.21)	(1.042)
2		11.2	(12.44)	(0.915)
	2	15.7	15.99	0.982
3		19.4	20.00	0.970
	3	23.5	24.11	0.975
4		28.7	28.83	0.995
	4	34.0	(33.39)	(1.018)
5		34.9	(34.81)	(1.003)
	5	36.6	(36.92)	(0.991)
6		40.8	40.90	0.998
	6	46.3	(45.94)	(1.007)
7		51.5	(50.74)	(1.015)
	7	56.3	56.19	1.002
8		61.3	61.21	1.001
	8	65.5	(65.23)	(1.004)
9		66.7	(67.35)	(0.990)
	9	68.2	(69.60)	(0.980)
10		74.4	73.78	1.008
	10	77.6	79.63	0.975
11		82.5	85.09	0.970
	11	89.1	90.98	0.979
		Ave. 11 features		0.987
		Ave. deviation		0.013

obviously much too short. This may be due to series termination errors, or it may be due to displacement of the average position of the hydrogen electron toward the bond, resulting, for the case of X-ray determinations of C-H bond distances, in typical values of 0.9-1.0 Å.

Application of Hedberg's method of calculating the boron radius to compounds of this sort,(14) using our set of interatomic distances, gives a value $R_B = 0.802$ Å, in excellent agreement with the average value of 0.799 Å calculated for the hydrides B_2H_6, B_5H_9 and $B_{10}H_{14}$. This result lends support to the conclusion that the parameter values are near to the correct ones. The X-ray parameters give $R_B = 0.75$ Å; evidently it is the short B-H distances which cause the small value.

The results of this electron diffraction investigation, together with the results of the independent X-ray investigation, definitely establish the structure of tetraborane as that shown in figure 4. As mentioned earlier, this model is pleasing when compared to the structure of other boron hydrides. The molecule is very similar to the end groups of the decaborane boat. The bonding about the central boron atoms is similar both to that about the apical atoms of decaborane and about the basal atoms of stable pentaborane. The end boron atoms are unique in having bonds to two other borons, but the total number, and directions, of the bonds is a common one. The tetraborane model may be cleaved into two equal parts resembling diborane molecules with a bridge hydrogen atom removed. The model also shows structural similarities to a model of unstable pentaborane described in the following part of this thesis.

Unstable Pentaborane: B_5H_{11}

The radial distribution curves for B_5H_{11} (Fig. 6) were calculated with modification functions $\exp(-aq^2)$ and $Aq^4 \exp(-a'q^2)$, just as for B_4H_{10}, and they resemble the B_4H_{10} curves rather closely. In particular, the strong B-B bond peak, at 1.81 Å, is somewhat broader than theoretical (0.11 Å vs 0.09 Å), indicating the possibility of two or more different bond distances, the broad B-H peak, at 1.27-1.51 Å, suggests the presence of bridge hydrogen atoms, and the prominent non-bonded B...B and B...H feature at 2.62-2.98 Å (here better resolved than for tetraborane) seems to contain B...B interactions in its outer component, at 2.98 Å.

There are now ten boron-boron interactions, of which from four to nine may be bonds. The number of the remaining boron-boron interactions which can possibly lie outside the 2.62-2.98 Å region is again limited, but not so severely as before; table 4 shows, for each possible combination of B-B bonds and B...B interactions within the 2.6-2.9 Å peak, the number of B...H interactions required to fill out the observed ratio of peak areas. The total number of boron-hydrogen interactions is fifty-five, of which at least eleven, and (assuming the existence of bridge hydrogen atoms) probably about sixteen, are bonds. This leaves about thirty-nine B...H terms to be accounted for, and we assume, as before, that not all of them will fall in the 2.6-2.9 Å region, and that as many as twenty-five or more falling outside of this region would be noticeable. This seems to indicate that models containing six, seven, or eight B-B bonds are the most promising ones.

Table 4

no. B-B	no. B...B at 2.62-2.98 Å	no. B...H at 2.62-2.98 Å
9	1	40
8	2	31
7	3	22
6	4	13
6	3	17
5	5	5
5	4	9
5	3	13
4	6	-4
4	5	0
4	4	4
4	3	8

The similarities of the tetraborane structure to the other borane structures suggest that the structure of unstable pentaborane should also show such similarities. The configuration shown in figure 5 is one which satisfies this condition as well as the radial distribution curve arguments: it was deduced from a study of the decaborane and tetraborane structures.* A theoretical

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*The same boron framework, but a different distribution of the hydrogen atoms was arrived at independently by Professor W. N. Lipscomb from a consideration of the stable pentaborane structure.

intensity curve (Fig. 6) was calculated for this model with the following parameter values: $B\text{-}B_{bond} = 1.81$ Å, $B_1\text{-}B_3 = B_2\text{-}B_4 = 2.96$ Å, $B_1\text{-}B_4 = 3.02$ Å, $B\text{-}H_{bond} = 1.20$ Å, $B\text{-}H_{bridge} = 1.42$ Å, ($a_{ij} = 0.00040$) $B_2 \ldots H_6(8) = 2.62$ Å, $B_1 \ldots H_8(4) = 2.62$ Å, and $B_2 \ldots H_{12} = B_3 \ldots H_{12} = 2.62$ Å: the bridge hydrogen atoms were assumed to be coplaner with the boron triangles. B...H interactions through more than one angle were not included in the calculation. Table 5 gives a comparison of the observed and calculated q values. The pleasingly close agreement between this curve and the visual intensity curve suggests that this structure, or one having the same boron skeleton, but a somewhat different distribution of hydrogen atoms,** may well be the structure of unstable pentaborane. In view of the large number of degrees of freedom involved, however, there can be no assurance that this is the only structure which will satisfy the intensity data.

It seems wise to postpone further work until the proposed structure has been verified (or ruled out) by the low temperature X-ray investigation of the crystal structure, which is being carried out by Professor W. N. Lipscomb. When the configuration is known, it may then be desirable to attempt a determination of the parameters.

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*For example, a small movement of a bridge hydrogen atom to a position near three boron atoms would add a mirror plane to the molecule and would result in all of the boron atoms having six-fold coordination.

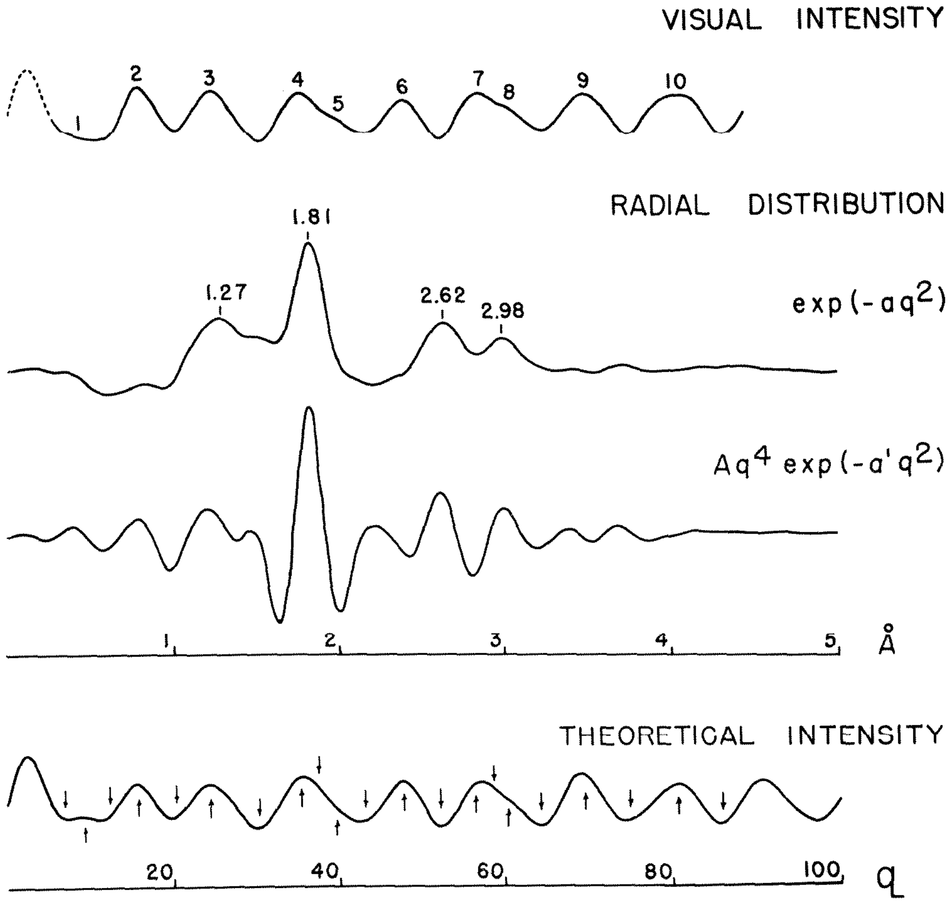


Fig. 6. Unstable pentaborane curves

Table 5

min.	max.	$q_{calc.}$	$q_{obs.}$	$q_{calc.}/q_{obs.}$
1		7.0	(6.59)	(1.062)
	1	8.6	(9.04)	(0.951)
2		11.1	(11.90)	(0.933)
	2	15.5	15.51	0.999
3		19.7	19.98	0.986
	3	24.2	24.32	0.995
4		30.1	30.19	0.997
	4	35.6	35.17	1.012
5		39.0	(37.30)	(1.046)
	5	40.2	(39.65)	(1.014)
6		42.4	42.91	0.988
	6	47.5	47.71	0.996
7		52.2	52.12	1.002
	7	56.9	56.29	1.011
8		59.2	(58.54)	(1.011)
	8	61.0	(60.16)	(1.014)
9		64.2	64.09	1.002
	9	69.1	69.53	0.994
10		74.2	74.78	0.992
	10	80.8	80.63	1.002
11		85.7	85.88	0.998
			ave. 14 features	0.998
			ave. deviation	0.006

Magnesium Boride

Until recently, the standard method for preparing the boron hydrides involved the acid hydrolysis of a "magnesium boride"(7). Powdered metallic magnesium and boric oxide were mixed in a thin-walled iron crucible, a current of hydrogen gas passed over the mixture, and the crucible heated until a glowing of the mixture indicated that the exothermic reaction had occurred. After cooling, the resulting dark brownish mass was powdered and hydrolyzed with 8-10 N phosphoric or hydrochloric acid to obtain the boron hydrides. An analysis of the boride mixture by Travers and Ray(15) indicated the presence of a magnesium boride of the composition MgB_2, but a subsequent study by Ray(16) was interpreted as showing that the boride was Mg_3B_2 and, furthermore, that this was the only stable boride of magnesium. According to Stock(7) it is this boride which is important for yielding the boron hydrides. Since the principal boron hydride resulting from the acid hydrolysis is B_4H_{10}, and since an intermediate in the formation of the "magnesium boride" has been isolated as the potassium salt $B_4O_6K_2$, Stock also postulates that magnesium boride contains B_4 complexes and consequently has the formula Mg_6B_4. Because of the interesting relationship between these possible B_4 groups and the B_4H_{10} molecule (the structure of B_4H_{10} was being investigated by the electron diffraction method at this time), the preparation and investigation of the crystal structure of magnesium boride was undertaken.

Although Ray(16) reported that metallic magnesium and crystalline boron would not react to form the boride, it was decided to try this method for the initial attempt. Commercial powdered boron (99.05%) was heated with a piece of clean magnesium (99.7%) larger than required by the stoichiometry of Mg_3B_2 in a magnesium oxide coated iron crucible to about 800° C for one hour. In order to minimize the formation of oxides and nitrides, a current of hydrogen was passed through the crucible throughout the heating period. After cooling, the excess magnesium, which was in the form of a metallic button, was removed. The product was a black powder, similar in appearance to the powdered boron, but noticeably darker in color. A small amount of this powder was introduced into a vessel containing 8<u>N</u> hydrochloric acid and a vigorous evolution of gas having the characteristic boron hydride odor was observed.

Samples of the powder were sealed into thin-wall soft glass capillaries about $\frac{1}{4}$ mm. in diameter and X-ray powder photographs were prepared in a Straumanis type Norelco powder camera of nominal radius $18/\pi$ cm. using nickel-filtered Cu K_α radiation. Two double film exposures were made and a second similar preparation of the compound was photographed in the same manner. The positions of the diffraction lines were accurately measured and the intensities were estimated visually. A film factor of 3.7 was used to relate the intensities of each pair of photographs. In addition, a check of the estimated intensities was made by comparison with photographs of $NaZn_{13}$, a compound for which excellent agreement had been obtained between observed and calculated intensities.

Values of $\sin^2\theta$ were calculated for all of the observed lines and 25 out of the 31 lines were indexed on the basis of a hexagonal lattice. Of the remaining six weak lines, one had a macro-crystalline appearance which was obviously different from the main pattern and corresponded in position to the strong $\underline{\underline{200}}$ reflection of elementary magnesium. The other five lines showed appreciable changes of intensity, relative to the main pattern, between the two different preparations and were therefore dismissed as belonging to an unidentified impurity.

Preliminary values of $\sin^2\theta_{100} = 0.0834$ and $\sin^2\theta_{001} = 0.0480$ were chosen and were then refined by a least squares treatment.(17) The observational equations were of the form:

$$(h^2 + k^2 + hk)\ d\sin^2\theta_{100} + \ell^2\ d\sin^2\theta_{001} = d\sin^2\theta_{hkl}$$

and the resulting normal equations were of the form:

$$\left[\sum_i w_i\ (h^2+k^2+hk)^2\right] \Delta\sin^2\theta_{100} + \left[\sum_i w_i\ell^2\ (h^2+k^2+hk)\right]\Delta\sin^2\theta_{001} = \sum_i w_i\ (h^2+k^2+hk)\ (\sin^2\theta_{hk\ell}^{obs.} - \sin^2\theta_{hk\ell}^{calc.})$$

and $$\left[\sum_i w_i{}^2\ (h^2+k^2+hk)\right] \Delta\sin^2\theta_{100} + \left[\sum_i w_i\ell^4\right]\Delta\sin^2\theta_{001} = \sum_i w_i\ell^2\ (\sin^2\theta_{hk\ell}^{obs.} - \sin^2\theta_{hk\ell}^{calc.}).$$

The weights, w_i, were set equal to $w_i'\ (\cos\theta\sin\theta)^{-2}$, with

w_i' an auxiliary weight depending on the physical characteristics of the line. Solution of the normal equations yielded the results:

$\Delta\sin^2\theta_{100} = -0.576 \times 10^{-4}$ and $\Delta\sin^2\theta_{001} = -0.709 \times 10^{-4}$.

With $\lambda = 1.5418$ Å for CuK$_\alpha$, the resulting hexagonal cell parameters and standard deviations are:

$$a_o = 3.0834 \pm 0.0003 \text{ Å}$$
$$c_o = 3.5213 \pm 0.0006 \text{ Å}.$$

The standard deviations were obtained from the residuals and coefficients of the normal equations in the least squares treatment.(17)

A cell of this size is certainly too small to contain the three magnesium and two boron atoms corresponding to the formula Mg_3B_2. Two alternatives are possible: either the formula approximates Mg_3B_2 and the structure is of a random type, or the composition differs from Mg_3B_2 with fewer atoms per unit cell. The similarity in the shape and size of the unit cell to that reported for AlB_2(18), pointed out to us by Dr. K. Hedberg, indicated that the two borides might be isomorphous, and structure factors were calculated on this basis using the atomic form factors of James and Brindley(19). The atomic positions are 1 Mg at (0,0,0) and 2 B at (1/3, 2/3, 1/2); (2/3, 1/3, 1/2). This structure consists of alternating layers of magnesium and boron atoms, the boron layers having twice the atomic density of the magnesium layers.

A comparison of $F_{obs.}$ and $F_{calc.}$ for all reflections within the sphere of copper radiation is given in table 6 along with observed and calculated values of $\sin^2\theta$. The $F_{obs.}$ values were reduced to an absolute scale by application of an empirical scale factor and the $F_{calc.}$ values include the temperature factor $\exp(-1.04 \sin^2\theta)$. For the unresolved (004, 203) doublet, values are given for $G^2_{obs.} = I/kLp$ and for $G^2_{calc.} = (mF^2_{calc.})004 + (mF^2_{calc.})_{203}$, where I is the observed intensity, k is the scale factor, L and p are Lorentz and polarization factors, and m is the multiplicity of the appropriate reflection. Excluding this doublet and the unobserved 003 reflection, the value for $R = \sum |F_{calc.} - F_{obs.}| / \sum |F_{obs.}|$ is 0.105.

The density of the boride was determined by the flotation method to be 2.62 g./cc., in agreement with the value 2.633 g./cc. calculated on the basis of the size and composition of the unit cell. The compound is thus established as being a magnesium boride of the composition MgB_2.

In view of this difference from Ray's result,$^{(16)}$ I attempted to find MgB_2 in the products of the reaction between Mg and B_2O_3. The preparation was carried out by the method described by Stock,$^{(7)}$ and an X-ray powder photograph of the product was made. The strong lines on the photograph agreed well in position and intensity with lines of magnesium oxide. Of the remaining complicated spectrum of weaker lines, two corresponded to two of the three strong lines of the MgB_2 pattern (002 and 110).

Table 6

hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	$F_{obs.}$	$F_{calc.}$
001	0.0478	0.0479	2.2	3.8
100	0.0834	0.0833	5.9	6.2
101	0.1313	0.1313	9.3	9.7
002	0.1918	0.1917	10.7	10.4
110	0.2501	0.2500	9.9	9.5
102	0.2753	0.2751	4.1	4.3
111	0.2980	0.2980	2.9	2.6
200	0.3334	0.3334	4.5	3.9
201	0.3809	0.3813	6.4	6.4
003	-	0.4313	-	2.0
112	0.4416	0.4418	6.8	7.2
103	0.5151	0.5147	4.6	5.4
202	0.5260	0.5251	2.0	2.8
210	0.5841	0.5834	3.5	2.6
211	0.6310	0.6313	5.3	4.7
113	0.6815	0.6814	1.2	1.2
300	0.7499	0.7501	5.0	5.0
203	0.7644	0.7647	$G^2_{obs.} = 184$	$G^2_{calc.} = 239$
004		0.7669		
212	0.7749	0.7751	1.6	1.9
301	0.7994	0.7980	1.2	1.2
104	0.8495	0.8502	1.2	1.6
302	0.9410	0.9418	2.9	4.2

The other strong line of MgB_2 (101) is degenerate in position with the strong 200 line of magnesium oxide. Thus there is some evidence that the boride formed in the reaction between Mg and B_2O_3 is MgB_2, rather than Mg_3B_2; furthermore, since in our preparation from the pure elements MgB_2 was formed even in the presence of a large excess of magnesium, it seems doubtful that Mg_3B_2 is a stable compound.

The complexity of the powder photographs of the product from the Mg-B_2O_3 reaction indicates that the actual reaction which occurs is considerably more complicated than the mere formation of magnesium boride and magnesium oxide, and that other products are formed in amounts comparable to MgB_2. According to Stock(7), the product contains, in addition to the boride, borates and hypoborates that are derived from oxides of boron lower than B_2O_3 that may play a part in the production of the boron hydrides.

Although Ray, in his investigations, used amorphous boron rather than boric oxide and, therefore, appreciably reduced the amount of these side products, the amorphous boron itself contained about 10% oxygen. His assumption that, upon completion of the reaction, this was either unchanged or in the form of a single magnesium boride appears unjustified. Lack of information on the compositions of the hypoborates and the details of Ray's result make it impossible to interpret his results in terms of the boride MgB_2.

MgB_2 is the ninth metallic boride now known to possess the AlB_2 structure. Besides AlB_2, the compounds TiB_2, VB_2, CrB_2, ZrB_2, NbB_2, and TaB_2 have been reported by Kiessling,(20) and Bertant and Blum(21) have reported on MoB_2. In table 7 there are given the lattice parameters and interatomic distances in these nine borides.

The existence of these nine isostructural borides containing metal atoms of differing properties affords an opportunity to attempt to correlate the observed internuclear separations on the basis of present-day theories of bonding in metals. On the basis of Pauling's equation relating bond number <u>n</u> with observed internuclear separation D_n,(22)

$$D_1 - D_n = 0.6 \log n ,$$

where D_1 is the sum of the single-bond radii of the two atoms involved in the bond, there is, for any value assigned to the single-bond radius of the metal atom in a compound MB_2, only one value for the single-bond radius of boron which will result in the total calculated valences of the atoms being equal to the number of valence electrons present in the compound. Furthermore, the single-bond radius assigned to the metal atom should be consistent with the valence calculated for that atom and may differ from the normal valence in view of electron transfer. This is the method used by Hedberg(13) in his discussion of the boron hydrides and related boron compounds.

The single-bond radii for the metal atoms (other than magnesium and aluminum) were chosen according to Pauling,(23) with appropriate corrections for any assumed electron transfer and resultant change in the d- character of the bonds. The single-bond radii for magnesium and aluminum were calculated from the empirical formula $R_1 = 1.759 - 0.055z - 0.488p$, where z is the number of outer electrons in the neutral atom and p is the p-character of the bonds, arrived at by interpolating between Pauling's values. In this regard, the value chosen for d- or p-character was an interpolation between values for neighboring atoms, thus the bond orbitals of titanium, which has an assumed valence of 4.4 (the excess over 4.0 being attributed to electron transfer), were given a d-character interpolated between the values 0.27 and 0.35 assigned to the bond orbitals of neutral titanium and neutral vanadium respectively.

In table 7 there are given the final calculated values for the boron single-bond radius for each of the compounds, as well as the valences of each atom and the calculated bond numbers. The average for the single-bond radius of boron is 0.767 Å with an average deviation of 0.012 Å.

The single-bond radius of boron might be expected to vary directly with the valence of boron as is observed for other atoms. However, the least squares line, $R_1(B) = A + C(3-v_B)$, for the nine points gives $A = 0.768$ and $C = 0.005$ with the estimated standard deviation of

C, 0.018, so large as to make even the sign of C unreliable.

It should be pointed out that the calculated single-bond radius for boron in each compound is dependent upon the single-bond radius chosen for the other atom, which in turn is very sensitive to the amount of d-character assigned to the bond orbitals. Furthermore, there is little valid reason to suppose that the d-character of bond orbitals of charged atoms can be accurately determined by simple interpolation. Thus the compounds NbB_2 and TaB_2, which give evidence of little electron transfer, yield single-bond radii for boron very close to 0.768 Å; the compounds with an appreciable amount of electron transfer, which necessitates an interpolation of p- or d-character, show larger discrepancies.

The observed pattern of electron transfer is in agreement with Pauling's theory(24) that boron, although a hypoelectronic atom, tends to transfer electrons to the less electronegative and likewise hypoelectronic atoms magnesium and aluminum. The tendency for boron to donate electrons decreases as the hypoelectronic character of the other atom decreases (and its electronegativity increases) until the buffer atom chromium, with an electronegativity approximately equal to that of boron, is able to transfer a large amount of charge to boron, thereby increasing the latter's bonding power without great loss to its own.

The observed value for the single-bond radius of

Table 7

	Mg	Al	Ti	V	Cr	Zr	Nb	Mo	Ta
a_o (A)	3.0834	3.00	3.030	2.998	2.969	3.170	3.088	3.05	3.078
c_o (A)	3.5213	3.245	3.223	3.057	3.066	3.532	3.304	3.113	3.265
B-B (A)	1.780	1.73	1.749	1.731	1.714	1.830	1.783	1.76	1.777
B-M (A)	2.503	2.37	2.378	2.309	2.300	2.543	2.431	2.35	2.413
M-M (A)	3.083	3.00	3.030	2.998	2.969	3.170	3.088	3.05	3.078
v_M	3.22	3.60	4.38	4.68	4.80	4.46	4.98	5.34	5.00
v_B	2.39	2.70	2.81	3.16	3.60	2.77	3.01	3.33	3.00
r_1 (M)	1.298	1.236	1.292	1.254	1.233	1.393	1.349	1.326	1.339
r_1 (B)	0.774	0.756	0.750	0.753	0.777	0.797	0.771	0.758	0.767
n (B-B)	0.410	0.433	0.385	0.422	0.541	0.404	0.397	0.392	0.394
n (B-M)	0.191	0.234	0.275	0.314	0.329	0.258	0.303	0.360	0.308
n (M-M)	0.154	0.132	0.181	0.152	0.145	0.229	0.224	0.170	0.215

boron, 0.77 Å, is considerably shorter than the value reported by Hedberg(14) for the boron hydrides and related compounds. This discrepancy is probably to be expected in view of the great dissimilarity in the types of structures involved. The AlB_2 structure, with well defined layers and consequent anisotropy of bonding, would be open to strain and deformation of bonds. Even more important is the high coordination of boron (9-fold) compared to that in the more covalent type structures. Professor V. Schomaker pointed out that this effect is obvious from the results of Hedberg's calculation.

A complete study of other metal-boron compounds would throw some light on the bonding characteristics of boron.

Beryllium Boride

The formation of boron hydrides by acid hydrolysis of the product of heating magnesium with boric oxide appears to occur in similar yield if beryllium is used in place of the magnesium.(7) If the first process involves a magnesium boride, the second presumably involves a similar beryllium boride; on the other hand, the beryllium atom is so small compared to the other metal atoms of the MB_2 series that the composition BeB_2 is rather unlikely. Altogether, an attempt to prepare a beryllium boride and study its crystal structure seemed desirable.

A mixture of approximately equal weights of commercial powdered boron (99.05%) and powdered beryllium metal (premium grade) was heated with a gas-oxygen torch to about 1400° C for several minutes in a beryllium oxide crucible under a current of helium. (Because beryllium is so very toxic, all operations of handling and heating were carefully performed in a hood.) The resulting inhomogeneous mass contained particles having a copper appearance. Some of these particles were powdered and sealed in a thin-wall soft glass capillary tube, and an X-ray powder photograph was prepared by the method described for magnesium boride. The photograph indicated the existence of at least two phases, as evidenced by the macro-crystalline appearance of a rather small number of lines in addition to a complex spectrum of smoother lines. The positions of the lines were measured and those having the macro-crystalline appearance were indexed on the basis of a face-centered cubic unit cell with $a_o \approx 4.66$ Å. The intensities of the lines indicated a fluorite type of structure. Further preparations were made from varying relative initial amounts of beryllium and boron, and X-ray powder photographs were taken of the products in each case. For most of the experiments, a quartz tube was used in place of the beryllium oxide crucible. It was found that the maximum yield of the cubic phase occurred for an initial atomic ratio of beryllium to boron between 2:1 and 1:1, presumably closer to the 2:1 value; the other lines appeared to be due to one or more phases having a higher beryllium content. Several unsuccessful attempts were made to prepare the cubic phase in essentially pure form for reliable determinations of composition and density. The positions and intensities of the cubic lines were measured on several photographs by the methods described for magnesium boride. Least squares refinement on the $\sin^2\theta_{hk\ell}$ values led to the result $a_o = 4.6583 \pm 0.0017$ Å; the observed and calculated values of $\sin^2\theta_{hk\ell}$ are given in table 8.

Structure factors were calculated for a fluorite structure of the composition Be_2B, with 8 Be at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. $(3/4,3/4,3/4)$ + F.C. and 4 B at $(0,0,0)$ + F.C., using the atomic form factors of James and Brindley.(19) The resulting moduli showed approximate agreement with the observed intensities and the signs, together with the observed moduli $|F_{obs.}|$, led to the plot of $\rho(x,x,x)$ *vs* x shown in figure 7. In addition to the expected peaks at the origin and $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, there is a peak at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

about one-quarter as high as the main peaks. This position has eight beryllium neighbors at a distance of 2.02 Å and cannot, therefore, contain a beryllium atom with a single-bond radius of 1.07 Å. It therefore appears that, in addition to eight beryllium atoms and four boron atoms, the unit cell contains approximately one other boron atom randomly distributed among the four positions $(\frac{1}{2},\frac{1}{2},\frac{1}{2}) +$ F.C. giving a composition approximating Be_8B_5. Structure factors were calculated on the basis of this composition and a comparison with the observed values is given in table 8. The reliability factor, $R = \sum \left| F^2_{calc.} - F^2_{obs.} \right| / \sum \left| F^2_{obs.} \right|$, is 0.15.

Table 8

hkl	$\sin^2\theta^{obs.}_{hkl}$	$\sin^2\theta^{calc.}_{hkl}$	$F^{2\ obs.}_{hkl}$	$F^{2\ calc.}_{hkl}$
111	0.0822	0.0822	100	57.2
200	0.1094	0.1095	10	11.6
220	0.2192	0.2191	542	534
311	0.3003	0.3012	26	28.5
222	0.3269	0.3286	4	18.4
400	0.4372	0.4382	374	426
331	0.5201	0.5203	27	21.6
420	0.5474	0.5477	7	15.6
422	0.6572	0.6473	405	332
(333) (511)	0.7392	0.7394	31	18.7
440	0.8765	0.8764	235	274
531	0.9586	0.9585	18	17.1

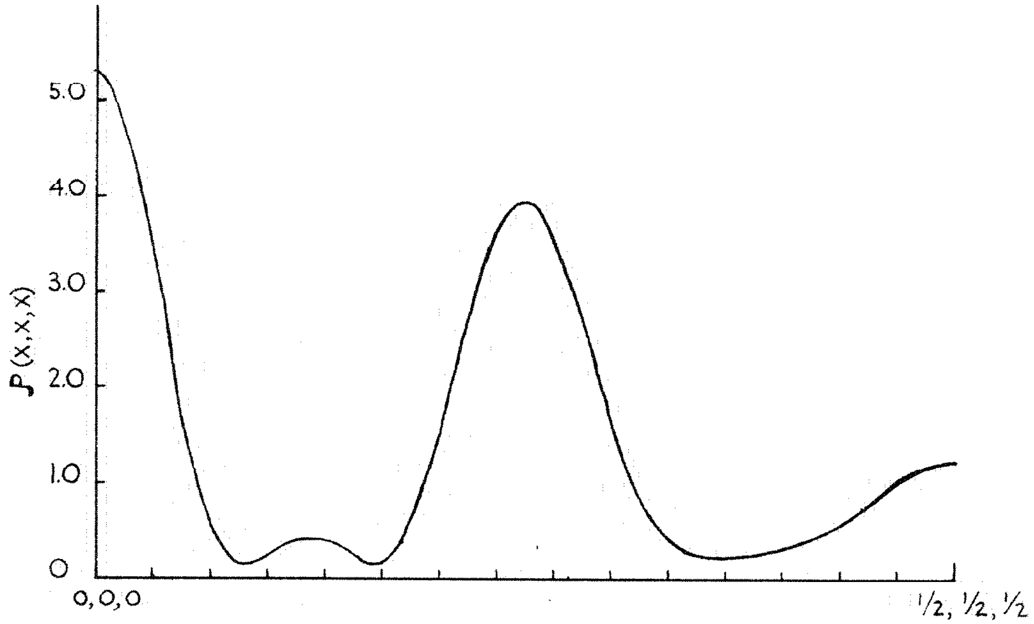


Fig. 7. Electron density along the body diagonal of the beryllium boride unit cell.

The densities of several of the copper colored pieces, as measured by flotation, ranged from 1.96 to 2.20 g./cc. ; the calculated density for five boron and eight beryllium atoms in the unit cell is 2.071 g./cc. An 81.2 mg. sample of the copper colored material was dissolved in concentrated HCl and analyzed. The beryllium was precipitated with ammonium hydroxide, filtered using Whatman #40 paper, ignited to constant weight and determined as the oxide. Sodium hydroxide was added to the filtrate and the ammonia expelled by boiling. After adding bromine, the solution was boiled further to insure conversion of all of the boron to borate. The pH was adjusted to correspond with a comparison solution containing an approximately equivalent amount of boric acid; methyl red was used as the indicator. Mannitol was added and the solution was titrated with standard 0.1 N sodium hydroxide to a phenolphthalein end point. The result of the analysis was

$$\text{Be} = 70.5 \text{ mole } \%$$

$$\text{B} = 22.2 \text{ mole } \%$$

The remaining 7.3% was material which was insoluble in concentrated HCl, and was probably boron of some form; however, the indication from the powder photographs that the boride was not a pure phase made any attempts to obtain further information unworthwhile. The composition Be_8B_5 corresponds to 61.5 mole % beryllium and 38.5 mole % boron. Indications from the powder photographs that other phases may comprise as much as 30% of the sample, and evidence that these phases are on the high beryllium side of Be_8B_5, make the results of the analysis not unreasonable. Direct determination of the exact composition will require a sample of much higher purity than we have so far been able to obtain; Professor Pol Duwez has kindly consented to investigate the possibility of obtaining improved samples at the Jet Propulsion Laboratory.

The tentative structure, of approximate composition Be_8B_5, is truly an interesting one. Of the many metallic borides which have been studied, the great majority contain boron frameworks of some sort, such as chains, hexagonal nets, or three dimensional networks of joined octahedra. The boron-boron distances in these borides have lengths in the range 1.7-1.8 Å, and appear strong compared to the boron-metal and metal-metal bonds. Moreover, a given structure type is stable over a rather wide range of different metal atoms, as for example in the MB_2 series. Presumably, it is the ability of boron to form the frameworks in these compounds which is chiefly responsible for their formation and stability.

Beryllium carbide, Be_2C, has been studied(25) and found to have the fluorite structure. One may, therefore, consider the structure of Be_8B_5 to be a compromise between the desire of beryllium to form the fluorite arrangement and the desire of boron to form some sort of network containing boron-boron bonds. The boron does in the proposed

Be_8B_5 structure, but not in the related ideal fluorite arrangement. Also, in contrast to Be_8B_4, Be_8B_5 has almost identically the same number of valence electrons per unit cell as Be_8C_4, and this may be significant. We can only conclude that both points of view lend credibility to a fluorite structure with about one extra boron atom per unit cell.

Copper Boride

Our work on magnesium boride led to an interest in Marsden's report of a copper boride Cu_3B_2.(26) Marsden heated a mixture of amorphous boron and metallic copper in a porcelain crucible for 3 - 4 hours to a temperature above the melting point of copper. The brittle, yellowish product resembled iron pyrites in appearance, and, by qualitative analysis, contained copper, silicon, and boron; the density was 8.116 g./cc. Quantitative analysis for copper and silicon, together with the assumption that the sample was a mixture of silica and a copper boride, then led to the formula Cu_3B_2.

Our attempt to prepare this boride was carried out in a similar manner, a current of helium being passed over the sample during the heating period. In addition to unreacted copper and boron, the product contained small particles of a silvery substance. These particles were brittle and had a density of about 8g./cc.

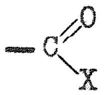
X-ray powder photographs, prepared from a crushed sample of the substance, turned out to be identical with photographs obtained later from a sample of the copper silicide Cu_5Si. It was also noticed that fragments of the substance changed, on standing in air, until they had the appearance of pyrite. The powder, when heated to 100° C for a short time in the presence of air, also developed this yellow color.

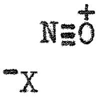
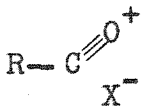
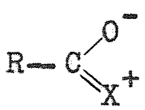
The X-ray photographs and similarities in the preparation and properties of our sample to Marsden's Cu_3B_2, together with the failure of other attempts to prepare a copper boride,(27,28) seem to indicate that both preparations are actually copper silicide, or possibly a ternary Cu-Si-B compound.

Additional attempts using the electric arc furnace of the Jet Propulsion Laboratory were unsuccessful, and it appears that no copper boride can be formed by a direct union of the two elements.

II SOME OTHER STRUCTURAL STUDIES

Formyl Fluoride

The desire to understand the properties of the  group (such as high reactivity, dipole moment, and bond force constants) has led to investigations of the molecular structures of several acid halides and related compounds. An electron diffraction study of the acetyl halides by Allen and Sutton(29) showed the fluoride to have a carbon-fluorine bond length in agreement with that in methyl fluoride, but the acetyl chloride, bromide, and iodide showed long carbon-halogen bond lengths as compared to the corresponding methyl halides. Moreover, this lengthening of the halogen bond was observed to increase in the sequence from fluoride to iodide. Investigations of carbonyl fluoride (30) and phosgene(31) showed no appreciable lengthening of the halogen bonds, but the C = O distance was found to be slightly shorter than in aldehydes and ketones.

Similar cases of the lengthening of bonds to halogen atoms has been observed for the nitrosyl halides, and it has been postulated(32) that this is due to the contribution of the resonance form  $\underset{^{-}X}{N\equiv\overset{+}{O}}$ to the ground state of the molecules. Schomaker(31) and Allen and Sutton(29) have discussed the possibility of a similar type of resonance in the acid halides, the resonance structures  and  both contributing significantly to the ground state. A discussion of the properties of phosgene in terms of this resonance has been given by Schomaker.(31) The investigation of the structure of formyl fluoride was undertaken to obtain further experimental information on these compounds.

The sample of formyl fluoride was prepared by the method of Nesmejanow and Kahn(33) from formic acid, sodium fluoride, and benzoyl chloride. The crude product was collected in a dry ice trap, distilled under vacuum at -40° C, and then redistilled at -35° C. The boiling point of the distillate was measured and found to be -39° C, considerably lower than the value of -24° C for pure formyl fluoride. A small portion of the sample was introduced into water and tested with silver nitrate. The resulting white precipitate indicated the presence of a considerable quantity of chloride, probably formed as a result of the reaction

$$\phi\mathrm{COCl}+\mathrm{HCOOH} = \phi\mathrm{COOH}+\mathrm{HCl}+\mathrm{CO}.$$

In order to remove this hydrogen chloride, the sample was distilled twice through a trap containing sodium fluoride. The resulting product boiled at -24° C and gave no precipitate with silver nitrate.

The sample was photographed by the methods previously described and visual intensity curves (Fig. 8) were drawn independently by two observers (M. Jones and K. Hedberg). Comparisons were made with photographs of formic acid, which were very similar to those of formyl

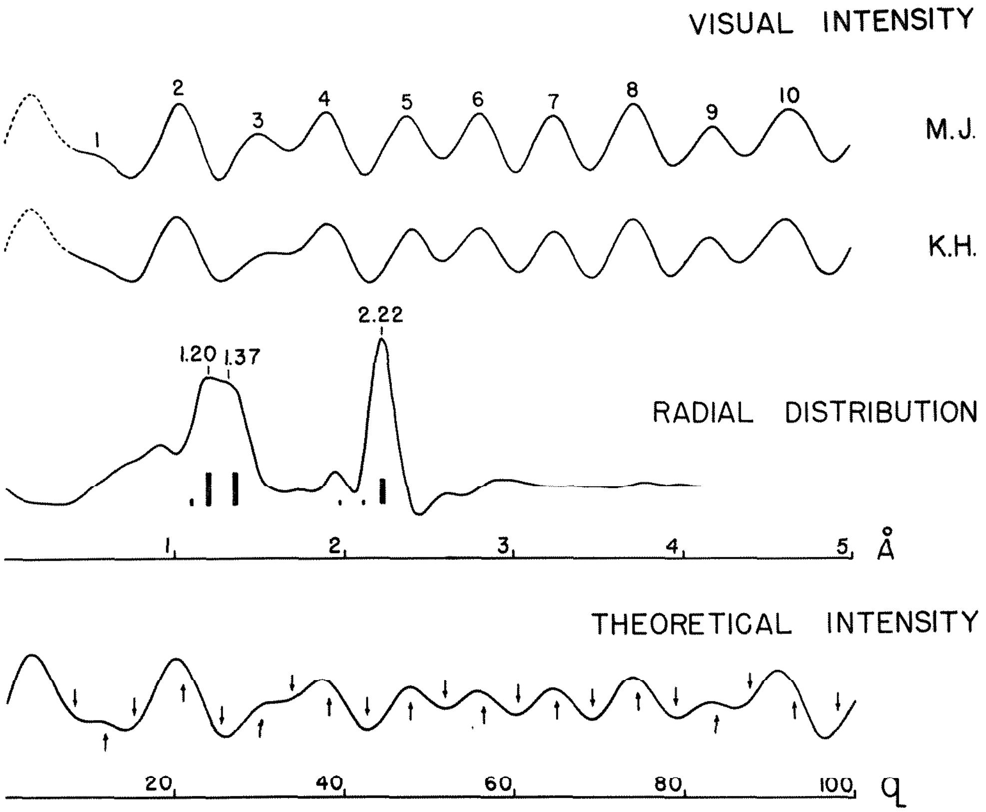


Fig. 8. Formyl fluoride: theoretical intensity curve for R = 1.133 and ∠ = 121°

fluoride, and the small differences were taken into account in drawing the visual intensity curves. The two visual curves show excellent agreement on all points except the relative depths of minima 5, 7 and 8, where, re-examination of the photographs showed, curve K.H. is to be preferred. A radial distribution curve was calculated (Fig. 8) using the $\exp(-aq^2)$ modification function. The strong, barely resolved, first radial distribution peak indicated C=O and C-F distances of about 1.20 Å and 1.37 Å, respectively. The peak at 2.22 Å corresponds to the O...F interaction and indicates a bond angle of 119.3°.

Theoretical intensity curves were calculated for models having parameters in the range C-H = 1.09 Å (assumed), ratio C-F/C=O = 1.072 to 1.197, and angle O=C-F = 117° to 127°. These curves showed that a model having ratio and angle of 1.133 and 121° was near to the correct one (Fig. 8).

It was considered worthwhile to apply a least squares method, as devised by W. Hamilton,(34) for the purpose of refining the parameter values. In order to conveniently utilize the curves already calculated, the parameters were chosen as ratio C-F/C=O, S = average of C-F and C=O (scale parameter) and ratio F...O/S. Variation of the C-H distance had been shown to produce a negligible effect on the curves and was, therefore, not included as a parameter in the least squares adjustment. The observational equations contained twofold and threefold comparisons of intensity, in addition to the positions of the maxima and minima. The methods of Hamilton(34) and Ibers and Schomaker(35) were used for assigning weights to the observations (table 9). The observational equations were transformed to the normal equations in the usual manner.(17) Solution of the normal equations yielded the results

$$\Delta R = 0.00179$$

$$\Delta S = -0.00984$$

$$\Delta F\ldots O/s = 0.00676 \text{ Å}.$$

The resulting final parameter values were

$$\text{ratio } C-F/C=O = 1.13457$$

$$S = 0.99016$$

$$F\ldots O/S = 2.24676 \text{ Å},$$

or, in terms of the interatomic distances,

$$C-F = 1.353 \text{ Å}$$

$$C=O = 1.192 \text{ Å}$$

$$F\ldots O = 2.225 \text{ Å}$$

corresponding to an O=C-F angle of 121° 47'.

The standard deviations and correlation coefficients of the parameters were obtained(17) by calculating the moment matrix M, from which the appropriate matrix M', corresponding to standard deviations and correlation coefficients in the interatomic distances, was calculated. An additional contribution to the standard deviation in the scale factor due to errors in the measurement of the

Table 9

Amplitude Comparisons

minima	$\sqrt{w_i}$	maxima	$\sqrt{w_i}$
2- 3	5	3- 4	2
3- 4	2	4- 5	7
3- 5	3	5- 6	10
5- 6	2	6- 7	7
6- 7	4	7- 8	5
7- 8	7	8- 9	3
8- 9	10	9-10	3
9-10	5	2,4- 3	2
10-11	2	2,5- 4	7
2,5- 3	5	4,6- 5	10
3,5- 4	2	5,7- 6	10
3,6- 5	4	6,8- 7	7
5,7- 6	4	7,9- 8	3
6,8- 7	5	8,10- 9	3
7,9- 8	10		
8,10- 9	7		
9,11-10	4		

Positional Comparisons

minima	$q_{obs.}$	$\sqrt{w_i}$	maxima	$q_{obs.}$	$\sqrt{w_i}$
3	25.45	8	2	20.26	8
4	33.68	0	3	30.23	0
5	43.05	40	4	37.94	16
6	51.75	24	5	48.31	8
7	60.88	32	6	56.17	8
8	69.46	32	7	65.01	24
9	78.77	12	8	74.33	40
10	86.72	4	9	83.31	12
11	97.53	4	10	91.88	8

electron wave length, the camera distance, and the film factor, was estimated to be 0.004, and was included in the treatment by assuming $\sigma_s(\text{final})^2 = \sigma_s(\text{L.S.})^2+(0.004)^2$. The resulting moment matrix in terms of interatomic distances was

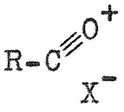
$$M' = \left(\begin{array}{ccc} \text{C=O} & \text{C-F} & \text{F...O} \\ 0.316 & 0.266 & 0.661 \\ 0.266 & 0.359 & 0.705 \\ 0.661 & 0.705 & 1.587 \end{array}\right) \times 10^{-4}$$

It has been estimated by Hamilton(34) that a satisfactory estimate for the limit of error would be given by 2σ. The final parameter values and limits of error obtained from this investigation are then

$$\text{C=O} = 1.192 \pm 0.011 \text{ Å}$$
$$\text{C-F} = 1.353 \pm 0.012 \text{ Å}$$
$$\text{F...O} = 2.225 \pm 0.025 \text{ Å}.$$

The average deviation in $q_{calc.}/q_{obs.}$ for 12 features is 0.004.

The bond distances in formyl fluoride are comparable to those in other acid fluorides and related compounds, and are much closer to the normal values than the distances in the corresponding chlorides, bromides, and iodides. The observed lengthening of carbon halogen bonds, increasing in the sequence from fluoride to iodide, may be accounted for by considering the contribution of the resonance forms



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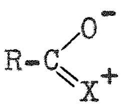

II

postulated by Schomaker(31) and discussed by Allen and Sutton(29) (although the latter authors did not seem very enthusisastic). As one proceeds from fluorine to iodine the tendency to form the ion decreases, but the double-bond forming power decreases at an even greater rate. If, in the case of the fluoride, the contribution of the resonance forms I and II is about equal, the contribution of II would be expected to decrease more rapidly than that of I as the fluorine atom was replaced by chlorine, bromine, and iodine atoms, resulting in an increase in the carbon-halogen bond lengths in the manner that is observed. No quantitative treatment of this effect is possible due to a lack of sufficiently accurate data on the relative tendencies of the halogens to form resonance structures of the sort proposed; however, on a qualitative basis the explanation appears to be a reasonable one.

Ozone

This investigation was initiated at a time when the value of the bond angle in ozone was in considerable doubt, and even the obtuse-angled structure was doubted in some quarters. In this laboratory, an electron diffraction determination(36) had led to an angle of 127°, but a subsequent spectroscopic study(37) seemed to indicate a considerably smaller value, at least if the bond length were at all close to the electron diffraction value of 1.26 Å. Reinvestigation by electron diffraction was surely in order.

The ozone was prepared from commercial tank oxygen using a silent discharge ozonizer. The resulting gas, containing about 6% ozone, was passed through three dry ice traps and condensed in a sample bulb at -192° C. When a sufficient quantity of liquid had condensed, the ozonizer was disconnected, and the liquid ozone-oxygen mixture was pumped on with a mechanical vacuum pump at -192° C. A mercury manometer was used to indicate the progress of the oxygen removal. After the vapor pressure of the liquid became unobservably small, the pumping was continued for several minutes, the sample bulb stopcock was closed, and the ozone was allowed to vaporize. Electron diffraction photographs were then prepared, within about a half hour, in the normal manner, with the sample at room temperature. The initial ozone pressure in the bulb was estimated to be in the range 100-200 mm. Hg.

The photographs were very much superior in appearance to the old ones.

A visual intensity curve was drawn. Theoretical intensity curves were calculated for models having bond angles in the range 115-127°. In addition, curves were calculated for various admixtures of oxygen. On the basis of 100% ozone, the theoretical intensity curves indicated a bond angle of about 118°. Unfortunately, however, the oxygen impurity could not be determined from the appearance of the photographs since it, and a certain simultaneous increase of bond angle and decrease of bond length, in the ozone model, have closely similar effects on the theoretical intensity curves. It was necessary, therefore, to determine by chemical methods the purity of ozone samples prepared and handled in a like manner to those used for obtaining the photographs.

Samples of ozone were prepared by the method previously described, and the bulb plus sample was weighed at room temperature. Approximately thirty minutes after the ozone was first vaporized, the sample bulb stopcock was opened for a short time and some gas allowed to pass through the electron diffraction nozzle into an evacuated flask containing a neutral potassium iodide solution. This solution was acidified with HCl, and the ozone determined by titrating the liberated iodine with a standard thiosulfate solution. The total quantity of gas represented by the analysis was determined by reweighing the sample bulb after the experiment. The values obtained for four such experiments ranged from 48% to 58% ozone by weight, indicating a decomposition so rapid under the conditions employed as to make the actual composition of the diffracting gas stream for any particular photograph quite uncertain. Although the procedure for the analysis was as similar as possible to the electron diffraction experiment, a considerable amount of time elapsed between the two, and there is, therefore, no assurance that the 50% ozone value was the same as the value at the time the photographs were prepared. This result discouraged any further attempts to interpret this first group of photographs.

Further studies were carried out on the effect of keeping the gaseous ozone samples at -80° C. The procedure was the same as before except that a manometric method was used for determining the total amount of gas in the sample bulb. The ozone content of such samples was found to drop from an initial value of 88 mole % to about 83 mole % after thirty minutes at -80° C.

Attempts to photograph samples kept in this manner were unsuccessful because of troubles with the electron diffraction equipment. It is to be hoped that good photographs eventually will be obtained.

During the course of the present investigation, the results of two independent microwave studies of ozone(38,39) were reported. The two determinations gave bond angle values of 116.5°-117° and 116°49'±30', and bond distance values of 1.27 Å and 1.278 ± 0.003 Å. These values are in reasonably good agreement with our estimate on the basis of the impure ozone photographs.

Copper Silicide: Cu_5Si

Attempts to prepare a copper boride (see page 51) by heating copper filings with powdered boron in a porcelain crucible yielded some small silvery particles. Samples of this material were crushed and X-ray powder photographs were prepared by the method described for magnesium boride. The positions of all of the lines on the photographs were measured, values of $\sin^2\theta$ were calculated, and the photographs were indexed on the basis of a primitive cubic unit cell with $a_o = 6.222$ Å. The intensities of all the lines were estimated visually by the multiple film technique described for magnesium boride.

Laue photographs of several small fragments were prepared, and, although none was a single crystal, one proved sufficiently simple to indicate the Laue symmetry: O_h. This fragment was oriented, and Weissenberg photographs of several zones were prepared. The Weissenberg photographs were useful for assigning approximate relative intensities to the components of degenerate powder lines, and for showing that the h00 reflections, most of which are degenerate with other reflections, occur only for $h = 4n$. This extinction, the O_h Laue symmetry, and the primitive unit cell limit the possible space groups to the enantiomorphic pair $O^6 - O^7$.

Up to this time, the silvery material had been assumed to be a copper boride; however, Professor Linus Pauling pointed out the similarity of the unit cell to that of Cu$_5$Si, which had been studied.(40) A comparison of the unit cell dimensions, and a comparison of our powder photograph with a reproduction of a photograph of the silicide, left little doubt that the sample was not a boride, but rather was Cu$_5$Si. Samples of Cu$_5$Si were then prepared from copper filings and powdered silicon metal, powder photographs were taken, and a comparison was made with photographs of the earlier preparations. These proved to be identical, thereby confirming the identity of the "boride" and the silicide.

According to Fagerberg and Westgren,(40) Cu$_5$Si is cubic, with $a_o = 6.211$ Å, and has the β-manganese structure.(41) Referred to the space group O^7, the 20 atoms per unit cell occupy the positions 12(d), with $x = 72^o$, and 8(c), with $x = 22^o$.* These twenty positions were reported to be occupied randomly by copper and silicon atoms, since the powder intensities of β-manganese, with only one kind of atom, and of Cu$_5$Si are similar. A random structure of this type is not so pleasing as an ordered

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*These positions are

12(d) = $3/8,\bar{x},3/4+x;\ 3/4+x,3/8,\bar{x};\ \bar{x},3/4+x,3/8;\ 7/8,1/2+x,1/4-x;\ 1/4-x,7/8,1/2+x;\ 1/2+x,1/4-x,7/8;\ 5/8,1/2-x,3/4-x;\ 3/4-x,5/8,1/2-x;\ 1/2-x,3/4-x,5/8;\ 1/8,x,1/4+x;\ 1/4+x,1/8,x;\ x,1/4+x,1/8,$

and 8(c) = $x,x,x;\ 1/2+x,1/2-x,\bar{x};\ \bar{x},1/2+x,1/2-x;1/2-x,\bar{x},1/2+x;\ 3/4-x,3/4-x,3/4-x;1/4-x,3/4+x,1/4+x;\ 1/4+x,1/5-x,3/4+x;\ 3/4+x,1/4+x,1/4-x.$

structure. Further study of the question seemed worthwhile, especially since an appreciable amount of X-ray data had already been gathered.

More silicide was prepared as before. Two pycnometric determinations on 10 g. samples yielded density values of 7.906 and 7.910 g/cc., and iodometric determinations(42) on nitric acid solutions of 0.2 g. samples gave values of 91.02 and 90.83 weight % copper.

Several X-ray powder photographs were prepared from the new samples and the positions of the lines were accurately measured. Reciprocal spacings ($1/d = q_{hkl} = \frac{2\sin\theta}{\lambda}$) were calculated from the positions of the powder lines. Analysis of a few lines in the back reflection region gave a tentative value of 0.160838 Å^{-1} for $1/a_o$. An absorption parameter K was introduced in conjunction with the absorption function of Nelson and Riley,(43) and a least squares refinement of $1/a_o$ and K was carried out. The observational equations were of the form

$$\sqrt{w_i}\frac{dq_i}{d(1/a_o)}\,\Delta(1/a_o) + \sqrt{w_i}\,q_i\cdot\tfrac{1}{2}\left(\frac{\cos^2\theta_i}{\sin\theta_i} + \frac{\cos^2\theta_i}{\theta_i}\right)K = \sqrt{w_i}\,(q_i^{obs.} - q_i^{calc.}),$$

where $(1/a_o)$ and K are the parameters to be solved for, q_i is the reciprocal spacing of the i^{th} line, and $w_i = w_i'/\cos^2\theta_i$ is the weight of the i^{th} line (where w_i' is an auxiliary weight based on the physical appearance of the line). The derivative $dq_i/d(1/a_o)$ is equal to $\sqrt{h^2+k^2+l^2}$.

Normal equations were obtained in the usual way(17) and solved for the two parameter values and expected standard deviations:

$$a_o = 6.2216 \pm 0.0003 \text{ Å}$$
$$K = 17 \times 10^{-4} \pm 1.8 \times 10^{-4}$$

The value 1.5418 Å was used for the CuKα wave length. The observed and calculated values of q_i are given in Table 10.

At about this point a new General Electric XRD-3 X-ray spectrometer was installed in the laboratory and, both to obtain accurate intensity data and to test the spectrometer, it was tried out on copper silicide. A sample of the silicide was powdered in a mortar to about 200 mesh, mixed with a binder prepared by diluting two drops of Duco cement with one cc. of acetone, and poured into a cellophane mold. After drying for two days, the resulting brick of sample, about 1.3 x 3.0 x 0.2 cm. in size, was freed from the mold, smoothed on one face with fine emery paper, glued to a strip of plastic, and mounted on the spectrometer. The X-ray intensity was then recorded over an angle range from 20° to 165° at a speed of 0.2°/minute. Nickel filtered CuKα radiation was used, and the recorder was calibrated in counts/sec. at several points both before and after the run. The intensity readings through the region of each observed reflection were then transferred from the logarithmic recorder scale to a linear scale and the areas measured.

But about half of the reflections proved too weak for satisfactory measurement by this method; for these the counting rate was measured directly with the scaler at small intervals throughout the region of each reflection, plotted on a linear scale, and integrated as before. The results were in general agreement with the visual estimates that had been made from the multiple-film powder photographs, the average deviation between the two sets being about 10%. No attempt was made to determine experimentally whether there was any partial orientation of small crystallites in the powder sample, in which case considerable errors might be introduced in the intensity measurements.

The Weissenberg data were used to separate the degenerate reflections, the intensities were reduced to $|kF_{obs.}|$ values by dividing out the multiplicity values and Lorentz and polarization factors, and were used, with signs calculated on the basis of Fagerberg and Westgren's random structure, to calculate the Fourier projection $\rho(x,y)$ (fig. 9). The peaks in this projection, which correspond to the 12(d) positions (A), are appreciably larger than those corresponding to the 8(c) positions (B). The ratio of the areas, 4:3, are accounted for by a structure in which the 12(d) positions are occupied solely by copper atoms while the 8(c) positions are occupied randomly by both copper and silicon atoms in a ratio of about 4.3 to 3.7. The density calculated on the basis of this structure, 7.855 g./cc., agrees well with the observed value 7.908 g./cc. The composition, $Cu_{4.41}Si$, is in excellent agreement with the value $Cu_{4.43}Si$ obtained from the analysis. The elongation of two of the three 12(d) peaks (A_1 and A_2) and the relative sharpness of the third seem to indicate that the atoms in these positions are undergoing asymmetric thermal vibration. Since an atom in the 12(d) position has twelve neighbors at an average distance of about 2.6 Å which are distributed fairly uniformly about it, there appears to be no reason to expect any preferred direction of vibration. The effect may be real, or it may be due to the use of the relatively inaccurate Weissenberg data in conjunction with the spectrometer data, or to errors in the spectrometer data due to a partial orientation of crystallites in the sample.

On the basis of the conclusions drawn from the electron density map, the structure factors were recalculated on the assumption that only copper atoms occupy the 12(d) positions, while both copper and silicon atoms randomly occupy the 8(c) positions in the proportions 4.3 to 3.7.

The scale factor and temperature factor were determined from a plot of log $\left[\sum m_i(F_i^{calc.})^2/I_{obs.}(L.p.)^{-1}\right]$ <u>vs</u> $(\sin\theta/\lambda)^2$, where $I_{obs.}$ is the observed intensity, L.p. are the Lorentz and polarization factors,

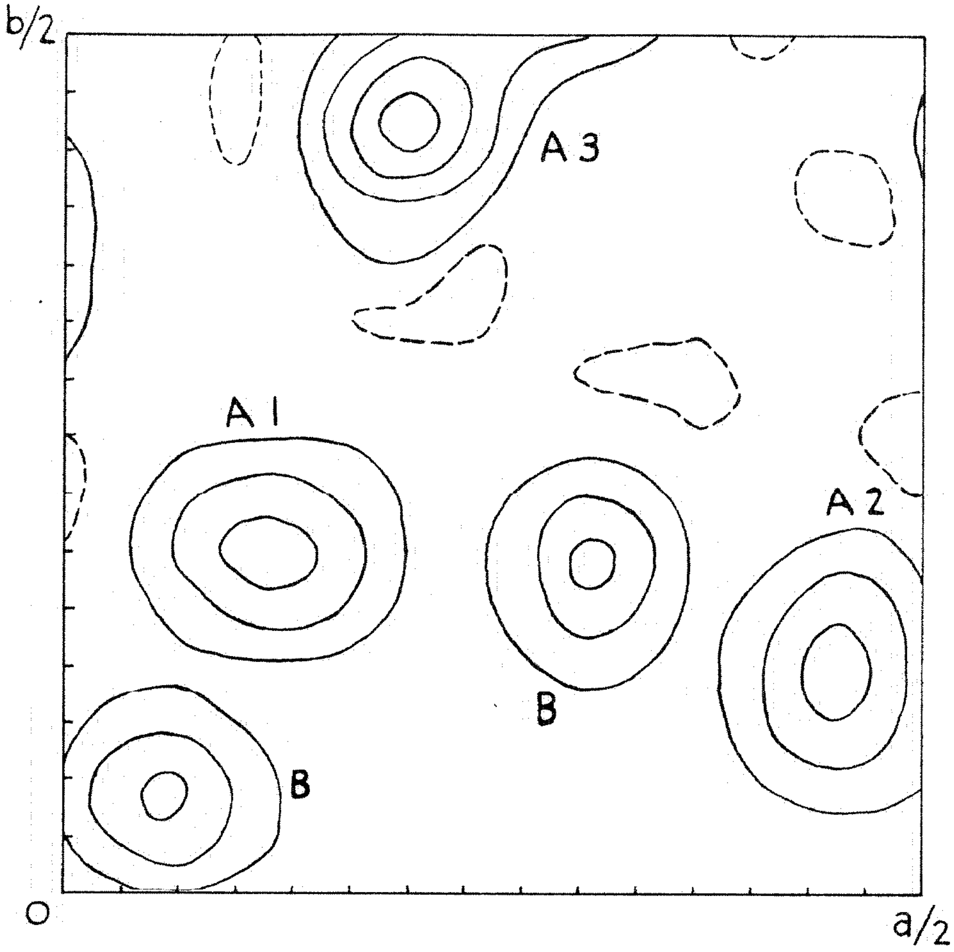

Fig. 9. Fourier projection of Cu_5Si on the xy plane. Contour interval is 4 electrons/$\mathring{A}^2$

m_i is the multiplicity of the i^{th} component of a degenerate reflection, and the sum is taken over the i components. The resulting value of B is 2.34 $Å^{-2}$. The resulting values of $F^2_{calc.}$ and $F^2_{obs.}$ are shown in Table 10. In the case of degenerate reflections the values of $G^2_{calc.} = \exp\left[-2B(\sin\theta/\lambda)^2\right]\sum m_i (F_i^{calc.})^2$ and $G^2_{obs.} = k^2 I_{obs.}/L.p.$ are shown. Excluding unobserved reflections, the quotient $\frac{\sum|F^2_{calc.} - F^2_{obs.}|}{\sum|F^2_{obs.}|}$ is 0.155.

This investigation has partially removed the complete randomness of Fagerberg and Westgren's structure. Further refinement of the structure on the basis of only the spectrometer data is contemplated. A least squares refinement of the positional parameters and composition, and study of the possible asymmetric temperature factor should be done.

Table 10

hkl	$q_i^{\text{calc.}}$	$q_i^{\text{obs.}}$	F^2_{hkl} calc. $\times 10^{-2}$	F^2_{hkl} obs. $\times 10^{-2}$
110	0.2295	-	0.3	-
111	0.2805	-	0.6	-
210	0.3614	0.3619	10.7	10.3
211	0.3957	0.3959	5.4	4.7
220	0.4566	-	0.7	-
221	0.4841	0.4841	224	193
310	0.5101	0.5101	144	143
311	0.5349	0.5353	72.6	59.5
222	0.5586	0.5584	8.6	4.2
320	0.5812	-	1.2	-
321	0.6031	0.6033	9.5	13.5
400	0.6445	-	3.6	-
(410) (322)	0.6643	-	(9.2)	-
(411) (330)	0.6835	0.6834	(669)	(737)
331	0.7021	0.7027	0.2	1.5
420	0.7203	0.7202	25.2	29.3
421	0.7380	0.7391	1.2	0.6
332	0.7553	0.7551	11.1	17.1
422	0.7888	0.7884	8.2	16.1
430	0.8050	0.8050	18.4	17.3
(431) (510)	0.8208	0.8206	(3220)	(4100)

Table 10 (Cont'd)

hkl	$q_i^{calc.}$	$q_i^{obs.}$	$F^{2\ calc.}_{hkl}\ x10^{-2}$	$F^{2\ obs.}_{hkl}\ x10^{-2}$
(333) ( ) (511)	0.8364	0.8363	(561)	(643)
(432) ( ) (520)	0.8667	0.8665	(2660)	(3087)
521	0.8815	0.8812	18.4	13.3
440	0.9103	-	3.7	-
(441) ( ) (522)	0.9243	-	(13.7)	-
(433) ( ) (530)	0.9382	0.9381	(197)	(358)
531	0.9509	0.9521	19.3	16.8
442	0.9653	0.9654	47.2	43.8
610	0.9785	0.9787	29.8	24.3
(611) ( ) (532)	0.9917	0.9916	(1020)	(999)
620	1.0174	-	2.9	-
(443) ( ) (540) ( ) (621)	1.0299	1.0304	(593)	(410)
541	1.0424	-	0.5	-
533	1.0546	1.0553	6.3	5.1
622	1.0668	-	0.4	-
(542) ( ) (630)	1.0788	1.0789	(512)	(474)

Table 10 (Cont'd)

hkl	$q_i^{calc.}$	$q_i^{obs.}$	$F^{2\ calc.}_{hkl}\ x10^{-2}$	$F^{2\ obs.}_{hkl}\ x10^{-2}$
631	1.0907	-	1.7	-
444	1.1141	-	0.6	-
632	1.1256	1.1256	11.3	9.3
(543) (550) (710)	1.1370	1.1369	(398)	(320)
(711) (551)	1.1369	-	(89.8)	-
640	1.1594	-	1.1	-
(641) (720)	1.1705	1.1705	(421)	(349)
(552) (633) (721)	1.1815	1.1816	(332)	(331)
642	1.2031	1.2031	12.8	12.8
(544) (722)	1.2137	1.2138	(480)	(470)
730	1.2244	1.2244	4.3	5.3
(553) (731)	1.2348	1.2348	(813)	(831)
(643) (650)	1.2555	1.2555	(859)	(1120)
(732) (651)	1.2657	1.2658	(710)	(727)
800	1.2859	1.2859	21.4	27.6

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The Use of Punched Cards in Molecular Structure Determinations. IV. Approximations to the Temperature Factor

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THE punched-card method[1] which we use for the functions $\Sigma_i G_i \sin y_i x$ that have to be evaluated in the course of diffraction studies of the molecular structures of randomly oriented molecules requires that the coefficients G_i be constants, independent of x. However, in the expression for the intensity of diffraction, in our case,[2]

$$I(s) = \Sigma'_{i,j} Z_i Z_j r_{ij}^{-1} \exp(-a_{ij}s^2) \sin r_{ij}s, \qquad (1)$$

these coefficients often include the so-called temperature factor $\exp(-a_{ij}s^2)$, which takes into account the vibrational variation or an effective vibrational variation of the interatomic distance about its mean value r_{ij}. The quantity a_{ij} is $\frac{1}{2}\langle\delta r_{ij}^2\rangle_{\mathrm{Av}}$ or, in order to make negligible the variation of some of the coefficients, an effective value $(\frac{1}{2}\langle\delta r_{ij}^2\rangle_{\mathrm{Av}} - a_0)$.

Previously, this variation has ordinarily been approximated by constructing the corresponding distribution of the form $\exp\{-(r-r_{ij})^2(4a_{ij})^{-1}\}$ and approximating the required integration over the distribution by a sum of equally spaced $\sin rs$ terms having constant coefficients taken from this curve with suitable normalization. But in the absence of any readily applicable analysis of the situation, the desire for accuracy has usually led to the use of more terms than are actually necessary. Therefore, it was decided to work out to known accuracy several economized representations of this type for general application.

In order to simplify the work, the equal spacing of terms was retained. Then, in terms of appropriate reduced units, the amplitudes and spacings of terms were adjusted so that the approximation differs from the desired value by no more than a fixed maximum amount for $s \leqslant s_{\max}$, with $s_{\max}$ as large as possible. This has been done for 2, 3, 4, and 5 term representations and for maximum errors of $\pm 2\frac{1}{2}$, ± 5, and ± 10 percent of the ideal initial amplitude, and the results have been arranged in a table. For each of the twelve cases, this table gives directly the a values that can be achieved with spacings of integral hundredths of an A (somewhat unhappily, continuous variation of a is not afforded), the amplitudes of the terms of the representation, and the maximum values of a for which it is accurate, respectively, to $s=20$ and $s=30$; a simple interpolation gives the maximum a values for other values of $s_{\max}$.

Use of the table has simplified the punched-card summation of Eq. (1) by reducing by 50 percent, on the average, the number of terms used to represent temperature factors. It has also reduced to almost nothing the considerable preparatory work which was previously involved in setting up the calculations.

Copies of the table and notes on its use have been prepared and are available upon request.

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* Contribution No. 1536.

[1] Shaffer, Schomaker, and Pauling, J. Chem. Phys. 14, 659 (1946).

[2] R. Spurr and V. Schomaker, J. Am. Chem. Soc. 64, 2693 (1942).

Table 11

Representations for approximating Ae^{-as^2}

$a \times 10^3$ *

$a_{max} \times 10^3$ $s \leq 20$	$s \leq 30$	max error	no of term	δ ** 0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	Amplitudes
2.11	0.94	2.5%	2	0.06	0.25	0.56	0.99	1.55	2.23	3.04	3.97	5.02	6.20	terms at $\pm\delta$ each having amp. = 0.488A
				7.50										
4.36	1.94	2.5%	3	0.03	0.11	0.25	0.45	0.70	1.01	1.37	1.79	2.25	2.80	central term amp. = 0.511A
				3.39	4.03	4.73	5.48	6.30	7.16	8.09	9.07	10.1	11.2	terms at $\pm\delta$ amp. = 0.232A
12.8	5.69	2.5%	4	0.17	0.67	1.51	2.69	4.20	6.05	8.24	10.8	13.6	16.8	terms at $\pm\delta$ amp. = 0.375A
				20.3	24.2	28.4	32.9	37.8	43.0	48.5				terms at $\pm 3\delta$ amp. = 0.113A
26.1	11.6	2.5%	5	0.06	0.26	0.58	1.02	1.60	2.30	3.14	4.10	5.18	6.40	central term amp. = 0.353A
				7.75	9.22	10.8	12.6	14.4	16.4	18.5	20.7	23.1	25.6	terms at $\pm\delta$ amp. = 0.238A
				28.2	31.0	33.9	36.8	40.0	43.3	46.7	50.2	53.8	57.6	terms at $\pm 2\delta$ amp. = 0.073A
3.10	1.38	5 %	2	0.07	0.28	0.63	1.13	1.76	2.54	3.46	4.51	5.71	7.05	terms at $\pm\delta$ each having amp. = 0.475A
				8.53	10.2	11.9								
11.3	5.01	5 %	3	0.03	0.14	0.31	0.55	0.86	1.23	1.68	2.19	2.77	3.42	central term amp. = 0.475A
				4.14	4.93	5.78	6.70	7.70	8.75	9.88	11.4	12.7	14.1	terms at $\pm\delta$ amp. = 0.238A
23.3	10.4	5 %	4	0.22	0.89	2.00	3.55	5.55	7.99	10.9	14.2	18.0	22.2	terms at $\pm\delta$ amp. = 0.339A
				27.8	32.0	37.5	43.5	49.9	56.8	64.1	71.9	80.0	88.8	terms at $\pm 3\delta$ amp. = 0.136A
31.8	14.1	5 %	5	0.07	0.26	0.58	1.04	1.62	2.34	3.18	4.16	5.26	6.50	central term amp. = 0.344A
				7.86	9.36	11.0	12.7	14.6	16.6	18.8	21.1	23.5	26.0	terms at $\pm\delta$ amp. = 0.232A
				28.6	31.5	34.4	37.4	40.6	44.0	47.4	50.9	54.7	58.5	terms at $\pm 2\delta$ amp. = 0.071A
5.30	2.36	10 %	2	0.09	0.36	0.80	1.42	2.22	3.20	4.36	5.69	7.21	8.90	terms at $\pm\delta$ each having amp. = 0.450A
				10.8	12.8	15.1	17.5	20.0						
15.8	7.03	10 %	3	0.04	0.17	0.38	0.68	1.06	1.52	2.07	2.70	3.42	4.22	central term amp. = 0.438A
				5.10	6.08	7.13	8.27	9.50	10.8	12.2	13.7	15.2	16.9	terms at $\pm\delta$ amp. = 0.231A
30.6	13.6	10 %	4	0.27	1.07	2.42	4.28	6.70	9.65	13.1	17.2	21.7	26.8	terms at $\pm\delta$ amp. = 0.321A
				32.4	38.6	45.3	52.5	60.3	68.6	77.4	86.8	96.7	107	terms at $\pm 3\delta$ amp. = 0.129A
40.3	17.9	10 %	5	0.08	0.32	0.73	1.30	2.03	2.92	3.98	5.19	6.57	8.11	central term amp. = 0.326A
				9.81	11.7	13.7	15.9	18.3	20.8	23.4	26.3	29.3	32.4	terms at $\pm\delta$ amp. = 0.220A
				35.8	39.3	42.9	46.7	50.7	54.8	59.1	63.6	68.2	73.0	terms at $\pm 2\delta$ amp. = 0.067A

*If an a value is given in the table, the corresponding representation is good at least as far as s = 10. For a given representation $a_{max} s_{max}^2$ = constant.

** δ is the distance in Å from r_{ij} (the center) to first side term. In each subtable of a values the first row corresponds to δ = 0.01, 0.02, ..., 0.10; the second to δ = 0.11, ..., 0.20; and the third, if present, to δ = 0.21, ..., 0.30.

Procedure for Using Table 11

I. Decide on the maximum error ($2\frac{1}{2}$, 5 or 10% of the initial amplitude) in the effective value of the temperature factor which will be tolerated.

II. By interpolation from the first two columns of the corresponding part of the table determine the representation needed to give this accuracy for $\underline{s} \leq \underline{s}_{max.}$ The distribution and amplitudes of the required terms may then be read from the last column. (If $\underline{s}_{max.}$ is either 30 or 20 simply pick the lowest value of $\underline{a}_{max.}$, in the appropriate column, which is greater than or equal to the desired $\underline{a}$ value.)

III. In the body of the table find the nearest value of $\underline{a}$ to the desired one and read out the corresponding value of $\underline{\delta}$.

Example: B-H bond: $a = 0.0016$; $A = 20$; $r = 1.17$;

$\underline{s}_{max.} = 30$.

I. Let the maximum error be $2\frac{1}{2}$% (corresponding to an error in A of $\frac{1}{2}$ part in 20).

II. According to column two, a three-term representation may be used and, from the last column, the central term will have amplitude 10 (rounded) and the terms at $\pm\delta$ amplitude 5 each.

III. The nearest value of $\underline{a}$ is 0.0018, giving $\underline{\delta} = 0.08$ Å.

Conclusion: The B-H term may be temperature factored with a maximum error, for $s \leq 30$, of $\frac{1}{2}$ plus the errors due to the rounding of the amplitudes and the fact that the representation actually corresponds to $a = 0.0018$ rather than $a = 0.0016$. The terms and amplitudes are the following:

r	A
1.09	5
1.17	10
1.25	5

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Propositions

1. The peak heights of radial distribution curves based on the modification function $M(q) = Aq^4 \exp(-a'q^2)$ are proportional to $(1/a')^{5/2}$. This is, therefore, a sensitive method for distinguishing between peaks due to rigid and to highly temperature-factored terms.

2. Stock suggests(1) that a magnesium boride is responsible for the formation of boron hydrides by the acid hydrolysis of a complex "magnesium boride" mixture. We have found evidence that MgB_2 is present in the mixture and that it yields boron hydrides on acid hydrolysis. A study of the relative yields of the hydrides obtained from equivalent quantities of MgB_2 and the complex mixture should show whether the boride is the sole active ingredient.

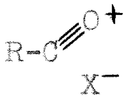
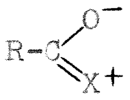
3. The investigation of beryllium boride showed that one or more high beryllium content phases exist. A determination of the Be-B phase diagram and an X-ray study of the high beryllium content phases should be made.

4. The possibility of using MgB_2 as a reducing agent for organic compounds should be investigated.

5. Paper chromatography provides a rapid and simple method of qualitative or semi-quantitative analysis of inorganic salts.
    a. I propose that a developer composed of secondary butanol, dioxane, and water is useful for effecting certain separations.
    b. I propose a possible mechanism for the action of this developer.

6. A Kelvin Water-Drop generator should be used for the purpose of demonstrating electrostatic induction to sophomore physics students.

7. The validity of Present's theory (2) that separate threshholds exist for symmetric and asymmetric fission should be checked by measuring the product yield curves for fission at frequent energy intervals ranging from thermal to several Mev.

8. The resonance structures  I and  II , proposed by Schomaker (3) in conjunction with a study of phosgene, provide a satisfactory qualitative explanation of the observed bond distances in the acid halides. In order to obtain a quantitative treatment, a measure of

the relative tendencies of the halogens to form these resonance structures is needed. The relative double-bond forming powers would provide a satisfactory measure of the tendency to form II, and could be obtained from an accurate redetermination of the bond distances in the halobenzenes.

9. Studies of the thermal polymerization of diborane(4,5) have shown the reaction to be of order 1.5.
   a. A mechanism for the polymerization, involving an unstable triborane intermediate, is proposed.
   b. A structure for this intermediate is proposed.

10. The "CalTech Alchemists", formerly the "CalTech Chemists", have fielded a baseball team for many years, and have recently expanded to include volleyball and basketball. Considering the available talent these teams have been respectable ones and have, more than once, "brought home the bacon." I propose that a subsidization of athletes by the Chemistry and Biology Departments would greatly improve the caliber of these teams and, as a consequence, result in more "bacon" for the Crellin trophy case.

References for Propositions

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