Acta Cryst. (1959). **12**, 503

The Crystal Structure of a Simple Rhombohedral Form of Boron

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(*Received* 27 *October* 1958 *and in revised form* 5 *January* 1959)

A new modification of boron, resulting from the pyrolytic decomposition of BI_3 on a heated surface (800 °C. to 1100 °C.), has been found to have a simple rhombohedral structure, with $a_0 = 5{\cdot}057$ Å and $\alpha = 58{\cdot}06°$, space group $R\bar{3}m$, $Z = 12$. The atomic parameters have been obtained from a single crystal using the precession method. The structure may be described as composed of units of nearly regular icosahedra in a slightly deformed cubic close packing. This requires the use of three-center or delta bonds, wherein two electrons are shared by three boron atoms at the vertices of an equilateral triangle.

Introduction

A new modification of boron with a simple rhombohedral structure has been found to result from the pyrolytic decomposition of BI_3 on a surface heated at 800 °C. to 1100 °C. (McCarty, Kasper, Horn, Decker & Newkirk, 1958). More recently, it has also been prepared by decomposition of boron hydrides (Robb, 1958), and, in addition, has been found to be present in some commercial materials. Tantalum, tungsten and boron nitride have all been used successfully as substrates on which decomposition of the iodide or hydride occurs. This form of boron is stable up to 1200 °C., and above 1500 °C. it transforms to the more complex rhombohedral form reported by Sands & Hoard (1957). In the range 1200 °C. to 1500 °C., a variety of complex diffraction patterns are produced; these have not been interpreted. The present paper is concerned only with the structure of the simple rhombohedral form of boron.

Experimental

The bulk of the material deposited on the substrate during pyrolytic decomposition of BI_3 is black, but red regions could be isolated in which there occurred clear red crystals (about $\frac{1}{4}$ mm. long).* Three-dimensional data for the structure determination were obtained from such a crystal using the precession method with zirconium filtered molybdenum radiation. All reflections were recorded on a series of zero-layer photographs to eliminate some of the variations in corrections needed. Intensities were evaluated by comparison with an intensity scale made from a reflection of the crystal. Lorentz and polarization factors were applied, but absorption in the sample was assumed to be negligible. A few photographs were taken of a second crystal, and results showed complete agreement with the first one.

All of the material deposited, both black and red, appears to be pure boron (except for a small amount of boride of the substrate element in some cases—e.g., TaB_2 from Ta substrate) with the same powder pattern as that obtained from crushed red crystals. The unit cell deduced from precession data accounted completely for the final indexing of the powder photograph. The structure is rhombohedral, with the following unit-cell dimensions derived from powder data:

rhombohedral:

$$a_0 = 5{\cdot}057 \pm 0{\cdot}003 \text{ Å}; \quad \alpha = 58{\cdot}06 \pm 0{\cdot}05°;$$

hexagonal:

$$a_0 = 4{\cdot}908 \pm 0{\cdot}003 \text{ Å}; \quad c_0 = 12{\cdot}567 \pm 0{\cdot}007 \text{ Å}.$$

Indices, interplanar spacings and intensities for a powder photograph taken with nickel-filtered copper radiation are given in Table 1.

The red crystals of boron, when examined by X-ray emission, showed about 0·04 weight per cent iodine but no other impurities with atomic number 13 or larger in concentration greater than 0·001 % (the limit of detection for the amount of sample available). The carbon content was determined by vacuum fusion analysis to be 0·003 %. The density of the crystalline material was found by Dr F. H. Horn to be 2·46 g.cm.$^{-3}$ as opposed to 2·33 g.cm.$^{-3}$ for the complex rhombohedral modification of boron. A value of 2·31 g.cm.$^{-3}$ is reported for tetragonal boron (Hoard, Hughes & Sands, 1958). The experimental density yields $Z = 12{\cdot}0$ for the number of boron atoms in the rhombohedral unit cell.

Structure determination

No systematic absences were observed for the rhombohedral cell, but the following rule was obeyed by the intensities:

$$\text{rhombohedral:} \quad I_{hkl} = I_{\bar{l}\bar{k}\bar{h}};$$
$$\text{hexagonal:} \quad I_{HK\cdot L} = I_{KH\cdot\bar{L}}.$$

The three possible space groups are $R32$, $R3m$ and

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* The isolation of the crystals was made by Dr F. H. Horn.

Table 1. *Powder pattern of simple rhombohedral boron*

(Cu $K\alpha$ radiation)

hkl	Hex. *HK·L*	*d* (Å)	Int.
111	00·3	4·247	45
100	10·1	4·066	100
110	01·2	3·544	2
211	10·4	2·545	70
$10\bar{1}$	11·0	2·479	10
221	01·5	2·180	4
210	11·3	2·132	4
$11\bar{1}$	02·1	2·113	55
200	20·2	2·029	<2
322	10·7	1·666	4
311	20·5	1·634	8
$20\bar{1}$	21·1	1·603	8
321	11·6		
332	01·8	1·482	8
310	21·4	1·438	15
$2\bar{1}\bar{1}$	30·0	1·424	8
333	00·9	1·403	4
331	02·7	1·376	8
320	12·5	1·359	10
300	30·3	1·346	15
$22\bar{1}$	03·3		
422	20·8	1·268	12
$20\bar{2}$	22·0	1·230	2
421	21·7	1·199	<2
$31\bar{1}$	22·3	1·178	4*
$21\bar{2}$	13·1		
411	30·6		
330	03·6		
$30\bar{1}$	31·2	1·161	<2
431	12·8	1·125	<2
443	01·11	1·105	2
$32\bar{1}$	13·4		
442	02·10	1·081	<2
$3\bar{1}\bar{1}$	40·1	1·060	<2
420	22·6		
$22\bar{2}$	04·2	1·048	2
444	00·12		
533	20·11	1·008	<2
400	40·4		
441	03·9	0·996	4
430	13·7	0·987	<2
521	31·8	0·944	2
544	10·13		
$41\bar{1}$	32·4	0·932	15
542	12·11		
531	22·9	0·922	<2
511	40·7	0·913	<2
$42\bar{1}$	23·5	0·909	2
$40\bar{1}$	41·3	0·906	2
$32\bar{2}$	14·3		
440	04·8	0·880	2
553	02·13		
541	13·10	0·860	<2
520	32·7	0·857	4
$22\bar{3}$	05·1	0·848	4
510	41·6		
$43\bar{1}$	14·6		
$4\bar{1}\bar{1}$	50·2	0·842	10
633	30·12		
552	03·12		
555	00·15	0·838	2
530	23·8	0·829	4
643	21·13		
644	20·14	0·827	<2
$33\bar{2}$	05·4	0·820	6
632	31·11		
$30\bar{3}$	33·0	0·818	4
622	40·10	0·811	<2
500	50·5	0·805	4
$31\bar{3}$	24·1	0·802	<2
$40\bar{2}$	42·2	0·796	<2
642	22·12		
654	11·15	0·793	<2
653	12·14	0·784	<2
$42\bar{2}$	24·4	0·778	2
551	04·11		

* Broad.

$R\bar{3}m$. Only the centrosymmetric $R\bar{3}m$ has been considered, and has been found to meet all demands of the data.

An icosahedral arrangement of boron atoms is found in boron carbide (Clark & Hoard, 1943) and in the tetragonal form of boron (Hoard, Geller & Hughes, 1951; Hoard, Hughes & Sands, 1958), and since the number of atoms in the rhombohedral unit cell for the present form of boron is 12, it was assumed for the first trial structure that each unit cell contained one unit of 12 boron atoms arranged on the vertices of an icosahedron. The three-fold axis of the icosahedron would, of course, have to coincide with the three-fold axis of the space group, that is, the [111] direction of the rhombohedron. Such an arrangement demands that the atoms lie on the mirror planes of the structure. They will, therefore, divide into two groups of six atoms each, in position

$$6h:\ x, x, z;\ x, z, x;\ z, x, x;\ \bar{x}, \bar{x}, \bar{z};\ \bar{x}, \bar{z}, \bar{x};\ \bar{z}, \bar{x}, \bar{x}$$

or, in the hexagonal cell, into two groups of eighteen atoms, in position

$$18h:\ \begin{matrix} x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z \\ \bar{x}, x, \bar{z};\ \bar{x}, 2\bar{x}, \bar{z};\ 2x, x, \bar{z} \end{matrix} + (0, 0, 0;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{3})$$

Thus, there are only four structural parameters.

Structure factor calculations for a regular icosahedron with B–B distances in the icosahedron equal to 1·80 Å were in good agreement with observed values and only small changes in parameters were indicated. An adjustment of parameters was made by trial and error methods. The values arrived at were

$$\mathrm{B_I}\ \text{in}\ 18h:\ x = 0{\cdot}120,\ z = \overline{0{\cdot}108}$$
$$\mathrm{B_{II}}\ \text{in}\ 18h:\ x = 0{\cdot}200,\ z = 0{\cdot}0255\,.$$

Using the Ibers (1957) scattering factor curve for boron, $R = \Sigma||F_c|-|F_o||/\Sigma|F_o| = 0{\cdot}144$.

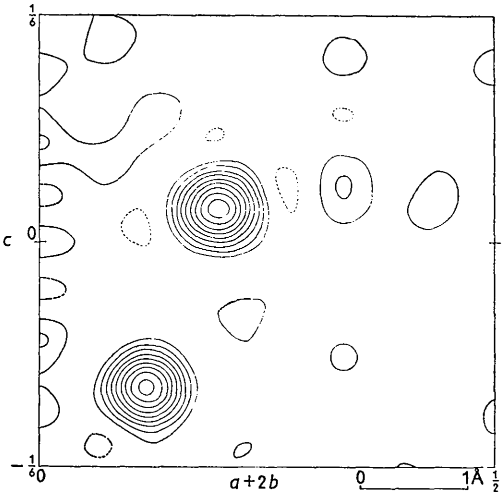

Fig. 1. Electron density, $\varrho(x, 2x, z)$, on a mirror plane. The contours are at equal intervals, the broken lines indicating negative contours.

Further refinement was attempted by Fourier methods. Since all four position parameters could be obtained from an electron-density section taken on one of the mirror planes of the unit cell, such a section was computed using signs from the trial structure calculations. The section is shown in Fig. 1. Since reflections at the limit of observable data were still quite strong, there is a fair amount of background variation on the map. Atom positions taken from this section are

$$\mathrm{B_I}\ \text{in}\ 18h:\ x = 0{\cdot}1177,\ z = \overline{0{\cdot}1073}$$
$$\mathrm{B_{II}}\ \text{in}\ 18h:\ x = 0{\cdot}1961,\ z = 0{\cdot}0245$$

or, in the rhombohedral cell

$$\mathrm{B_I}\ \text{in}\ 6h:\ x = 0{\cdot}0104,\ z = \overline{0{\cdot}3427}$$
$$\mathrm{B_{II}}\ \text{in}\ 6h:\ x = 0{\cdot}2206,\ z = \overline{0{\cdot}3677}\,.$$

When the structure amplitudes were recalculated with the new parameters, no sign changes occurred, except for a few reflections of very small amplitude and for

hkl	*HK·L*	F_o	F_c
$10\bar{1}$	11·0	16·8	−14·7
$2\bar{1}\bar{1}$	30·0	25·9	−29·5
$20\bar{2}$	22·0	22·4	23·8
$3\bar{1}\bar{2}$	41·0	3·1*	−2·4
$30\bar{3}$	33·0	35·3	33·3
100	10·1	23·9	25·3
$11\bar{1}$	02·1	33·9	−38·5
$20\bar{1}$	21·1	16·7	17·4
$21\bar{2}$	13·1	13·8	−15·8
$3\bar{1}\bar{1}$	40·1	6·1	−5·6
$30\bar{2}$	32·1	3·5*	1·4
$22\bar{3}$	05·1	28·1	26·6
$31\bar{3}$	24·1	5·6	5·5
$4\bar{1}\bar{2}$	51·1	14·9	−11·3
110	01·2	5·5	5·6
200	20·2	5·1	−5·1
$21\bar{1}$	12·2	2·9*	−1·2
$30\bar{1}$	31·2	8·4	8·6
$22\bar{2}$	04·2	14·9	−17·6
$31\bar{2}$	23·2	2·2	−2·3
$4\bar{1}\bar{1}$	50·2	5·4	5·4
$40\bar{2}$	42·2	6·6	−6·3
$32\bar{3}$	15·2	11·7	9·6
111	00·3	26·1	31·0
210	11·3	9·1	−7·7
300	30·3	26·9	28·2
$22\bar{1}$	03·3	29·7	−38·2
$31\bar{1}$	22·3	12·4	14·9
$40\bar{1}$	41·3	15·8	−12·2
$32\bar{2}$	14·3	8·5	6·7
$41\bar{2}$	33·3	3·8*	−1·8
211	10·4	31·3	−34·1
220	02·4	2·9	1·5
310	21·4	26·4	30·4
$32\bar{1}$	13·4	8·0	−7·9
400	40·4	15·5	15·9
$41\bar{1}$	32·4	33·6	−36·2
$33\bar{2}$	05·4	37·7	36·5
$42\bar{2}$	24·4	17·3	−12·4
$50\bar{1}$	51·4	7·5	5·5
221	01·5	11·1	−9·7
311	20·5	25·5	−24·9
320	12·5	25·3	26·9
410	31·5	3·5*	−1·8
$33\bar{1}$	04·5	3·2*	−2·2
$42\bar{1}$	23·5	14·0	−13·4
500	50·5	35·0	31·1
$51\bar{1}$	42·5	20·6	−17·8
$43\bar{2}$	15·5	2·4*	−2·1
222	00·6	2·4*	−0·6
321	11·6	4·3	−3·5
411	30·6	4·1	−3·1
330	03·6	6·8	6·2
420	22·6	8·3	8·1
510	41·6	8·6	−7·7
$43\bar{1}$	14·6	3·2	3·8
$52\bar{1}$	33·6	7·6	−8·5
322	10·7	17·7	−17·9
331	02·7	28·5	33·3
421	21·7	7·6	−7·5
430	13·7	8·5	8·5
511	40·7	4·3	3·5
520	32·7	25·8	−21·8
$44\bar{1}$	05·7	7·5	−4·5
$53\bar{1}$	24·7	2·7*	−1·3
332	01·8	24·5	26·6
422	20·8	35·0	−45·5
431	12·8	9·0	9·5
521	31·8	9·8	−10·7
440	04·8	17·8	−14·8
530	23·8	28·1	24·7
611	50·8	15·4	13·4
620	42·8	6·7	3·3
333	00·9	32·1	37·3
432	11·9	2·2	−3·3
522	30·9	3·2*	−2·9
441	03·9	27·2	−27·6
531	22·9	9·1	7·0
621	41·9	12·8	−9·9
540	14·9	12·7	9·9
433	10·10	1·9	3·0
442	02·10	5·6	6·5
532	21·10	3·2*	−3·8
541	13·10	11·4	−9·6
622	40·10	9·2	7·7
631	32·10	2·7*	−1·2
443	01·11	14·6	15·4
533	20·11	5·7	−6·9
542	12·11	15·9	−16·1
632	31·11	13·8	11·6
551	04·11	21·0	−20·9
641	23·11	25·6	23·3
444	00·12	18·0	−14·2
543	11·12	3·1	2·2
633	30·12	43·1	42·3
552	03·12	30·8	−30·7
642	22·12	6·3	−5·1
544	10·13	19·4	−18·8
553	02·13	22·8	18·3
643	21·13	9·3	8·2
652	13·13	3·1	−4·7
733	40·13	20·0	22·2
554	01·14	2·9*	−3·9
644	20·14	5·2	−2·9
653	12·14	5·2	2·8
555	00·15	36·4	−36·4
654	11·15	6·0	5·2
744	30·15	15·4	13·7
663	03·15	19·0	16·8
655	10·16	11·0	−11·0
664	02·16	32·6	34·2
665	01·17	18·2	13·5

* Indicates minimum observable amplitude for unobserved reflection.

which no intensity was observed. The *R* factor was reduced to 0·118. Observed and calculated structure factors are compared in Table 2.

An attempt to place observed intensities on an absolute scale by plotting log $(\Sigma_n f_n^2/\overline{I_{hkl}})$ against $(\sin\theta/\lambda)^2$ led to difficulties which are not fully understood. The straight line obtained, instead of having a positive slope—the effect of temperature motion—had a negative slope. This is believed to be due to a combination of experimental errors and inappropriateness of the available scattering factor. The possibility of extinction as a major source of the difficulty was considered but no satisfactory conclusion as to its role could be reached. The main experimental error could be associated with a decrease in size of the spots on the precession photographs with increasing θ. A negative slope could also be introduced if the *f*-curve used for boron is not applicable to this case. In fact, better agreement between observed and calculated structure factors is obtained with an empirical *f*-curve given by Nordman & Lipscomb (1953). However, since separation of experimental and *f*-curve errors is not possible for the present data, it was decided to stop the refinement at this stage. The absolute scale used is just that which gives best fit between observed and calculated structure factors, ignoring any temperature factor. An error in scale of Fig. 1, but maximum positions should be essentially correct. A program is being initiated to obtain single crystal data using a counter as detector. It is hoped that these data will lead to an evaluation of the *f*-curve, and reliable information about electron densities. It seems especially important to check whether the differences in contour shapes for the two boron atoms (Fig. 1) are real.

Discussion of the structure

The structure may be described as composed of units of nearly regular icosahedra in a slightly deformed cubic close packing. This structure also may be viewed as derived from that of boron carbide (Clark & Hoard, 1943) by omission of the carbon atoms from octahedral holes with a closer approach of icosahedra to form the 'three-center-bonds' as a replacement for three boron to carbon bonds. Fig. 2 is a view looking down the *c* axis of the hexagonal unit cell, showing the icosahedra at the corners of the cell. Icosahedra are also centered at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$. While this is a somewhat simple and satisfactory situation geometrically, it can be accomplished only by utilizing a new kind of bond—the three-center or delta bond—wherein two electrons are shared by three boron atoms at the vertices of an equilateral triangle. Bonds of this type

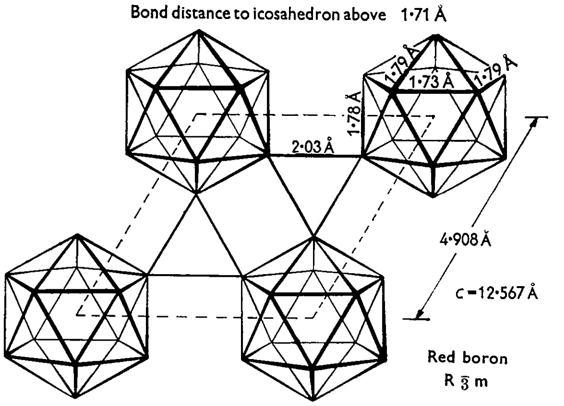

Fig. 2. The icosahedra at the corners of the unit cell as viewed from above. Interatomic distances are given for each type of bond.

Crawford & Lipscomb (1954). In the present boron structure, half of the atoms in an icosahedron are bound by conventional single bonds to atoms of other icosahedra. Each of the remaining atoms participates in a delta bond with two atoms from two different neighboring icosahedra.

Interatomic distances are shown in Fig. 2. Bonds within the icosahedron range from 1·73 to 1·79 Å, with the conventional bond to another icosahedron being slightly shorter, 1·71 Å. It would be reasonable to expect the delta bonds to be longer, and they are found to be 2·03 Å. It is very difficult to make an assessment of the reliability of the interatomic distances from the present data. We wish to defer considerations of exact distances until more complete and better information is obtained from further investigation. It is to be noted, however, that the distances above (except for the delta bonds) agree within 0·03 Å of the boron to boron distances in boron carbide.

The bonding in this boron structure can be rationalized on the basis of the Longuet-Higgins & Roberts (1955) treatment for an icosahedron of boron, which yields the result that thirteen orbitals, or twenty-six electrons, are used for internal bonding within the icosahedron. Since each boron atom has three valence electrons this leaves ten electrons to participate in bonds outside the icosahedron. The six conventional bonds take six electrons leaving four electrons for the delta bonds. A delta bond needs two electrons, or two-thirds of an electron per atom. Therefore, the six atoms in each icosahedron which participate in delta bonds need to contribute four electrons to these bonds, which is exactly the number available to them for bonding. Thus, a complete balance of electrons is attained.

This work was possible only because of the first successful synthesis of this material by Dr L. V. McCarty. We are indebted to him, and to Dr A. E. Newkirk for calling our attention to this very interesting material. Much of the non-crystallographic information is due also to Drs A. E. Newkirk and F. H. Horn. In addition, we wish to acknowledge many useful discussions with all three.

We are very grateful to Mr R. Lewinski for his capable assistance in obtaining the diffraction data.

References

Clark, H. K. & Hoard, J. L. (1943). *J. Amer. Chem. Soc.* **65**, 2115.

Eberhardt, W. H., Crawford, B., Jr. & Lipscomb, W. N. (1954). *J. Chem. Phys.* **22**, 989.

Hoard, J. L., Geller, S. & Hughes, R. E. (1951). *J. Amer. Chem. Soc.* **73**, 1892.

Hoard, J. L., Hughes, R. E. & Sands, D. E. (1958). *J. Amer. Chem. Soc.* **80**, 4507.

Ibers, J. A. (1957). *Acta Cryst.* **10**, 86.

Longuet-Higgins, H. C. & Roberts, M. de V. (1955). *Proc. Roy. Soc.* A, **230**, 110.

McCarty, L. V., Kasper, J. S., Horn, F. H., Decker, B. F. & Newkirk, A. E. (1958). *J. Amer. Chem. Soc.* **80**, 2592.

Nordman, C. E. & Lipscomb, W. N. (1953). *J. Chem. Phys.* **21**, 1856.

Robb, W. L. (1958). Private communication.

Sands, D. E. & Hoard, J. L. (1957). *J. Amer. Chem. Soc.* **79**, 5582.