THE CRYSTAL STRUCTURE OF BORAX*

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ABSTRACT

The crystal structure of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, has been worked out by means of the sign relationships of structure factors and by the triple Fourier series method. The unit cell has the dimensions of $a_0 = 11.858 \text{ \AA}$, $b_0 = 10.674 \text{ \AA}$, $c_0 = 12.197 \text{ \AA}$ and $\beta = 106^\circ 41'$, and the space group is C_{2h}^6 . There are four chemical units of composition, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in the unit cell. The coordinates of atoms were refined first by double Fourier series and the final triple Fourier series were carried out with 1763 terms. The standard deviations of coordinates finally obtained are $0.004 \text{ \AA}$ for sodium atoms, $0.02 \text{ \AA}$ for boron atoms and $0.02 \text{ \AA}$ for oxygen atoms. Hydrogen atoms have been located from the consideration on the electrostatic valencies directed to the oxygen atoms and the interatomic distances between oxygen atoms.

The structure of borax is composed of chains of regular octahedra formed by water molecules around Na, running parallel to the c-axis. These chains build up a sheet holding isolated groups of $\text{B}_4\text{O}_5(\text{OH})_4$ in between them through hydrogen bonds. These sheets are parallel to (100) and held together mainly by hydrogen bonds. The structure formula of borax may best be represented with the expression $\text{B}_4\text{O}_5(\text{OH})_4 \cdot \text{Na}_28\text{H}_2\text{O}$.

Introduction

There have remained many problems unsolved concerning the crystal structures of borate minerals and their mutual relations, among which borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is of most importance because of its practical use. In the present study, the crystal structure of borax was determined as part of a programme of investigation of the borate minerals at this Mineralogical Institute. The structure of this mineral is of special interest because of the possibility of finding the structural units of boron, oxygen and hydrogen atoms which or part of which might give clues to solve the structure of

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other borate minerals and because of the role played in the structure by the hydrogen atoms.

Since no assumption was made about the location of hydrogen atoms in advance, and they are omitted in calculating the structure factors, the term "oxygen atom" throughout this paper will be used comprehensively to include O^{2-} , OH^- and H_2O groups, without distinguishing between them, except where context makes distinction obvious.

Only few X-ray studies on borax have so far been reported. W. Minder⁸⁾ gave, in 1935, the lattice constants and space group of borax with other kindred minerals such as kernite ($Na_2B_4O_7 \cdot 4H_2O$) and tinalconite ($Na_2B_4O_7 \cdot 5H_2O$). Recently, José Ma. Font Tullot⁴⁹⁾ proposed its crystal structure on the basis of his X-ray data.

Experimental

As the material for this study, commercial borax was used after recrystallization. The lattice constants were determined first with the rotation photographs about the *a*-, *b*- and *c*-axes. The values obtained are $a_0 = 11.80 \pm 0.04 \text{ \AA}$, $b_0 = 10.67 \pm 0.05 \text{ \AA}$, $c_0 = 12.29 \pm 0.04 \text{ \AA}$ and $\beta = 106^\circ 35'$ (from goniometer measurement). At the later stage of the analysis, the redetermination of these values was carried out by the powder method with a "Norelco" X-ray diffractometer, quartz and silicon being chosen as the standard substances. The results obtained are $a_0 = 11.858 \pm 0.005 \text{ \AA}$, $b_0 = 10.674 \pm 0.005 \text{ \AA}$, $c_0 = 12.197 \pm 0.005 \text{ \AA}$ and $\beta = 106^\circ 41' \pm 2'$. In the unit cell, there are four chemical units of composition $Na_2B_4O_7 \cdot 10H_2O$. The space group is $C_{2h}^6 - C^2/c$, (*hkl*) being present only when $h+k=2n$, (*h0l*) only when $h=2n$ and $l=2n$ and (*0k0*) only when $k=2n$. These results are in good agreement with the ones previously described^{8,4)}.

Integrating Weissenberg photographs¹⁰⁾ were taken about the *a*-, *b*- and *c*-axes each up to the seventh layer by the multiple film technique. The samples used for this purpose were needle-crystals of about 0.5 mm. $\times$ 0.5 mm. in cross section and 1 mm. in length.

Throughout the experiments, $\text{CuK}\alpha$ radiation ($\lambda=1.542 \text{ \AA}$) was used.

The relative intensities were estimated visually and corrected for the Lorentz and polarization factors. No correction was made for absorption, nor for extinction. After the relative intensities were adjusted to the same scale, they were put on to the absolute ones by Willson's method¹¹⁾, which gave $B=1.40 \text{ \AA}^2$ for the temperature factor parameter. At the later stage of the analysis, these absolute intensities were found to be less by about 5% than the values expected from the correct structure.

Analysis

Since no structure of hydrated sodium borates has so far been determined, it was impossible to assume beforehand the probable arrangement of atoms for this mineral from the structural view-point, and the usual trial and error method could not be effectively employed. Moreover, since this mineral has a number of comparatively light atoms such as sodium, oxygen, boron and hydrogen atoms in the large unit cell, the application of the Patterson function was not expected to be effective. Therefore, the only probable way of attacking the problem was to make use of the sign relationships of structure factors.

This method was first applied to the two-dimensional reflections, that is, F_{hk0} 's, F_{k0l} 's and F_{0hl} 's. It was, however, impossible to obtain signs of reflections enough to produce a comprehensible Fourier projection.

Then all the three-dimensional observed structure factors, F_{hkl} 's which amount to about 1800 including 681 absent ones, were used for the sign determination. Since the origin of the unit cell may be shifted from one symmetry centre to another, it is possible to choose the signs of two structure factors at will in the space group of borax, C_{2h}^6 . Thus the positive sign was chosen for the reflections (170) and (735). It was found then that the signs of fifteen additional structure factors were uniquely determined from the following rela-

tion by Harker and Kasper⁵,

$$(U_{h,k,l} \pm U_{h',k',l'})^2 \leq (1 \pm U_{h+h', k+k', l+l'}) (1 \pm U_{h-h', k-k', l-l'}).$$

On the basis of the known signs, Cochran's relation²³, $S_H = S_K \cdot S_{H+K}$, was applied to all the structure factors whose U -values were more than 0.30. According to this procedure, the signs of 66 structure factors were expressed by +, - and two letter symbols a and b. For all the large structure factors not determined by the above methods and ones whose U -values were more than 0.20, Zachariasen's relationship¹², $S_H = (\overline{S_K \cdot S_{H+K}})$, was tested, and the signs of additional 144 reflections, as well as of the letters a and b, were deduced from the known ones.

Up to this stage, therefore, the signs of comparatively large 225 structure factors had been collected and it was expected that a three-dimensional Fourier synthesis based on these factors would give a good approximation to the correct structure. The three-dimensional

Fig. 1. The composite sections from $\rho(xyz)$ by the first triple Fourier series. The sections are projected on (010). The lower half only of $1/2a_0 \times 1/2c_0$ is shown. Contours are drawn at equal intervals of an arbitrary scale. The numbers give the height of each atom expressed as a percentage of the b_0 -translation.

Fourier summation was carried out over the points of $1/30 \times 1/30 \times 1/30$ of the unit cell. The Beever-Lipson strips were used for the calculation according to the next equation,

$$\rho_{xyz} = \frac{4}{V_c} \sum_{k=0}^{\infty} (J_{kxz} \cos 2\pi ky - j_{kxz} \sin 2\pi ky),$$

where $J_{kxz} = \sum_h \sum_{l=2n}^{l=2n+1} [F_{hkl} \cos 2\pi(hx+lz) + F_{hkl} \cos 2\pi(-hx+lz)]$

and $j_{kxz} = \sum_h \sum_{l=2n}^{l=2n+1} [F_{hkl} \sin 2\pi(hx+lz) + F_{hkl} \sin 2\pi(-hx+lz)]$.

The composite Fourier sections from $\rho(xyz)$ are given in Fig. 1, projected on to (010).

Since the heights of peaks at the centres of sodium, oxygen and boron atoms in the three-dimensional electron density map were expected to have the proportion of about 3:2:1 respectively as

Table 1. The atomic coordinates in borax.

Atoms	No. of atoms in the cell	Column 1			Column 2			Column 3		
		x/a_0	y/b_0	z/c_0	x/a_0	y/b_0	z/c_0	x/a_0	y/b_0	z/c_0
Na ₁	4	0	0	0	0	0	0	0	0	0
Na ₂	4	0	.847	.250	0	.843	.250	0	.845	.250
B ₁	8	.080	.347	.213	.082	.347	.215	.085	.345	.217
B ₂	8	.095	.460	.390	.098	.450	.397	.095	.454	.390
O ₁	4	0	.273	.250	0	.264	.250	0	.265	.250
O ₂	8	.143	.427	.305	.156	.420	.318	.154	.419	.314
O ₃	8	.025	.430	.125	.021	.437	.123	.018	.435	.123
O ₄	8	.158	.267	.170	.158*	.264	.167	.161	.269	.167
O ₅	8	.162	.493	.495	.165	.493*	.495*	.163	.511	.491
O ₆	8	.127	.850	.447	.123	.845	.453	.123	.846	.450
O ₇	8	.127	0	.195	.121	.002	.192	.125	.002	.196
O ₈	8	.117	.157	.462	.120	.163	.455	.119	.165	.459
O ₉	8	.118	.700	.167	.118*	.705	.178	.116	.707	.171

Column 1: The coordinates from the first triple Fourier series.

Column 2: The coordinates after two-dimensional refinements.

Column 3: The final coordinates from the second triple Fourier series.

observed in other crystals, it was easy to allot two sodium, nine oxygen and two boron atoms to the appropriate peaks in the diagram of the unsymmetrical domain of the unit cell. The results thus derived produced a structure which showed no contradiction to the known crystallographic knowledge such as the ionic radii of atoms and the coordination number of cations. These first approximate coordinates of atoms are given in Table 1, column 1.

Refinement of coordinates

Two-dimensional Fourier methods were employed as far as possible to refine the atomic parameters. All the signs of observed F_{hko} 's, F_{h0l} 's and F_{0kl} 's were derived from the above coordinates. Hartree's atomic scattering factors were used in this calculation with $B=1.40 \text{ \AA}^2$ for the temperature factor parameter. Two-dimensional Fourier diagrams projected on to (001), (010) and (100) were produced, the a-, b- and c-axes being divided into 60 parts. After several successive adjustments, all the signs ceased to change. The final coordinates of atoms whose peaks were resolved in the maps were given in Table 1, column 2. Throughout these processes, the original coordinates were used for oxygen atoms whose peaks overlapped in the maps and given in Table 1, column 2 with stars. The coordinates of boron atoms were adjusted in accordance with spatial requirements with oxygen atoms. The reliability factors based on these coordinates were 0.221 for F_{hko} 's, 0.194 for F_{h0l} 's and 0.253 for F_{0kl} 's, all present and absent reflections being counted.

The structure factors of general reflections, F_{hkl} 's, were then calculated with these coordinates. After calculation, it was found that the originally observed F -values should be increased by 5% to obtain the least values for the reliability factors, which reduced from 0.240 to 0.231 including present and absent reflections. With the corrected values of observed F_{hkl} 's, the three-dimensional Fourier series were recalculated, each axis being divided into 30 parts as earlier. The composite Fourier sections from $\rho(xyz)$ are projected on (010) and

(a)

(b)

Fig. 2. The composite sections from $\rho(xyz)$ by the second triple Fourier series. The sections are projected on (a) (010) and (b) (100). The lower halves only of $1/2a_0 \times 1/2c_0$ and $1/2c_0 \times 1/2b_0$ are shown in (a) and (b) respectively. Dots indicate positions of atoms according to the final parameters. Contours are drawn at 2, 4, 6, $e. \text{\AA}^{-3}$ for boron and oxygen atoms and 2, 4, 8, 12, $e. \text{\AA}^{-3}$ for sodium atoms.

(100) in Fig. 2. The position of each peak in the diagram was determined by Megaw's method⁷⁾, and was given in Table 1, column 3. As for hydrogen atoms, the positions were not determined in the diagram, though some swellings of electron density were observed at the places where hydrogen atoms would be expected as mentioned below.

In order to refine the temperature factor parameter, at this stage, the profiles through the peaks of sodium, oxygen and boron atoms were plotted by averaging the observed ρ -values of atoms of the same kind in the electron density map and compared with those calculated from Hartree's atomic scattering factors modified with the temperature factor parameter, $B=1.40 \text{ \AA}^2$. This indicated that the temperature factor parameter thereto adopted should be increased to $B=1.60 \text{ \AA}^2$. The structure factors of F_{hkl} 's were calculated again on the basis of the new coordinates and the revised temperature factor.

Only the calculated values of F_{hk0} 's, F_{h0l} 's and F_{h0l} 's are compared with the observed values in Table 2, the reliability factors of which are 0.190, 0.154, and 0.212 respectively. The reliability factor for all observed (present and absent) reflections is 0.220. In view of the facts that there are many absent reflections (not including space-group extinctions) which amount to 38% of all observed ones and that the hydrogen atoms were neglected in the calculation of the structure factors, this value of reliability factor seems to be sufficient to establish the structure under consideration.

Accuracy

In this work, systematic errors such as from extinction, absorption and termination effect in Fourier synthesis were not corrected. Therefore, in order to take account of these errors, the order of magnitude of the standard deviation of atomic coordinates was estimated from the following expression,

Table 2. Comparison of observed and calculated F -values.
Only F_{hkl} 's, F_{h0l} 's and F_{0kl} 's are given.

hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$
020	33	34	6.10.0	12	18	10.0.0	38	35
040	83	88	6.12.0	19	23	12.0.0	28	26
060	80	83				14.0.0	6	8
080	12	16	710	11	22			
0.10.0	12	21	730	22	19	002	37	— 34
0.12.0	38	50	750	30	31	202	54	— 53
			770	82	79	402	38	— 26
110	23	— 15	790	15	— 26	602	27	— 25
130	24	— 31	7.11.0	8	7	802	22	— 22
150	38	39				10.0.2	15	— 14
170	133	142	800	134	128	12.0.2	24	— 21
190	—	— 3	820	—	0			
1.11.0	31	29	840	12	8	004	90	90
1.13.0	11	11	860	38	44	204	163	211
			880	—	4	404	26	33
200	94	118	8.10.0	6	— 2	604	31	— 30
220	19	16				804	11	7
240	6	— 6	910	64	61	10.0.4	44	44
260	27	27	930	—	3	12.0.4	37	30
280	—	— 4	950	26	29			
2.10.0	20	— 20	970	50	53	006	98	92
2.12.0	10	7	990	9	8	206	21	— 14
						406	86	— 83
310	41	48	10.0.0	38	35	606	42	30
330	32	30	10.2.0	—	3	806	43	32
350	36	42	10.4.0	—	— 3	10.0.6	14	— 6
370	—	— 2	10.6.0	30	29	12.0.6	—	2
390	31	29	10.8.0	8	— 4			
3.11.0	—	6	10.10.0	—	— 17	008	—	8
3.13.0	—	14				208	87	86
			11.1.0	12	— 12	408	96	106
400	143	— 157	11.3.0	6	2	608	24	22
420	27	30	11.5.0	11	— 5	808	—	— 5
440	8	— 9	11.7.0	—	— 3	10.0.8	27	32
460	43	— 42	11.9.9	—	9			
480	10	4				0.0.10	—	6
4.10.0	—	— 7	12.0.0	28	26	2.0.10	19	18
4.12.0	—	— 5	12.2.0	—	12	4.0.10	25	— 14
			12.4.0	14	15	6.0.10	29	— 18
510	26	— 27	12.6.0	12	— 12	8.0.10	18	— 16
530	—	— 9	12.8.0	—	11			
550	10	13				0.0.12	12	10
570	17	9	13.1.0	22	— 21			
590	—	1	13.3.0	6	4	2.0.12	12	10
5.11.0	8	— 6	13.5.0	—	1	4.0.12	6	17
			14.0.0	6	8	6.0.12	45	37
600	134	154				0.0.14	26	— 27
620	39	22	200	94	118	2.0.14	—	— 14
640	53	60	400	143	— 157			
660	19	— 11	600	134	154	20 $\bar{2}$	10	— 6
680	26	22	800	134	128	40 $\bar{2}$	10	— 6
						60 $\bar{2}$	16	8

80 $\bar{2}$	19	15	061	—	0	067	29	28
10.0. $\bar{2}$	13	10	081	—	11	087	30	27
12.0. $\bar{2}$	—	5	0.10.1	—	14	0.10.7	—	2
14.0. $\bar{2}$	—	9	0.12.1	40	38	0.12.7	—	1
20 $\bar{4}$	156	—158	002	37	— 34	008	—	3
40 $\bar{4}$	—	4	022	83	91	028	42	46
60 $\bar{4}$	140	160	042	12	— 8	048	28	24
80 $\bar{4}$	74	69	062	87	76	068	—	8
10.0. $\bar{4}$	18	— 16	082	—	11	088	—	7
12.0. $\bar{4}$	—	4	0.10.2	—	10	0.10.8	—	10
14.0. $\bar{4}$	47	42	0.12.2	—	5			
20 $\bar{6}$	98	—102	003	—	—	009	—	—
40 $\bar{6}$	68	— 76	023	22	19	029	—	4
60 $\bar{6}$	62	64	043	62	— 59	049	22	13
80 $\bar{6}$	60	— 45	063	16	— 22	069	—	2
10.0. $\bar{6}$	73	— 67	083	—	9	089	—	2
12.0. $\bar{6}$	—	2	0.10.3	—	4	0.10.9	—	7
14.0. $\bar{6}$	—	3	0.12.3	—	2			
20 $\bar{8}$	58	58	004	90	90	0.0.10	—	6
40 $\bar{8}$	134	134	024	16	24	0.2.10	78	86
60 $\bar{8}$	67	70	044	14	14	0.4.10	42	41
80 $\bar{8}$	10	6	064	105	110	0.6.10	—	4
10.0. $\bar{8}$	34	30	084	62	58	0.8.10	—	12
12.0. $\bar{8}$	47	52	0.10.4	—	8	0.10.10	27	27
14.0. $\bar{8}$	20	23	0.12.4	36	37			
2.0. $\bar{10}$	40	— 46	005	—	—	0.0.11	—	—
4.0. $\bar{10}$	—	7	025	8	— 20	0.2.11	—	2
6.0. $\bar{10}$	31	33	045	70	58	0.4.11	31	26
8.0. $\bar{10}$	10	— 13	065	31	34	0.6.11	—	11
10.0. $\bar{10}$	—	— 12	085	15	— 24	0.8.11	—	6
12.0. $\bar{10}$	18	22	0.10.5	—	9			
14.0. $\bar{10}$	—	13	0.12.5	—	6	0.0.12	12	10
2.0. $\bar{12}$	10	— 6	006	98	92	0.2.12	12	— 14
4.0. $\bar{12}$	31	34	026	47	46	0.4.12	36	36
6.0. $\bar{12}$	49	41	046	85	93	0.6.12	—	8
8.0. $\bar{12}$	—	6	066	—	1	0.8.12	22	20
10.0. $\bar{12}$	25	25	086	18	15			
12.0. $\bar{12}$	35	46	0.10.6	56	52	0.0.13	—	—
14.0. $\bar{12}$	—	13	0.12.6	—	9	0.2.13	—	5
001	—	—	007	—	—	0.4.13	—	5
021	107	—128	027	34	34	0.6.13	—	0
041	48	— 48	047	19	— 21	0.0.14	26	— 27
						0.2.14	18	12
						0.4.14	—	10

$$\sigma(x) = -\sigma\left(\frac{\partial\rho}{\partial x}\right) / \left(\frac{\partial^2\rho}{\partial x^2}\right)_{\text{peak}}.$$

Cochran¹⁾ has shown that $\sigma(\partial\rho/\partial x)$ may be evaluated by determining the slope of the background resulting from the synthesis, and this has the advantage of taking account of all sources of error. In this

expression, the dominator simplifies to $-2p\rho_{\text{peak}}$, if the atom has a Gaussian distribution near the peak. Surveys of the background remote from any atom gave

$$\sigma(\partial\rho/\partial x) \approx \sigma(\partial\rho/\partial y) \approx \sigma(\partial\rho/\partial z) \approx 1.5e. \text{\AA}^{-4},$$

and the value of p for each atom was determined by comparison of $\rho = \rho_0 \exp(-pr^2)$ with the ρ -values of the atom in the electron density map, giving 6.1 for sodium, 4.1 for oxygen and 6.0 for boron atoms. These values gave 0.004 $\text{\AA}$ for sodium, 0.012 $\text{\AA}$ for oxygen and 0.013 $\text{\AA}$ for boron atoms as the standard deviation, $\sigma(x)$.

The standard deviation in three dimensions, $\sigma(r)$, was estimated from $\sigma(x)$ of each atom. No error is associated with Na_1 occupying the special position (0, 0, 0). For Na_2 occupying the special position (0, y , 1/2), however, the error for its y -parameter must be considered and it is 0.004 $\text{\AA}$ same as $\sigma(x)$. The standard deviation $\sigma(r)$ for oxygen and boron atoms was estimated as 0.021 $\text{\AA}$ and 0.022 $\text{\AA}$ respectively.

Location of hydrogen atoms

As mentioned above, it was impossible to find the location of ten independent hydrogen atoms in the unit cell and to distinguish between O_2^- , OH^- and H_2O groups only by means of the electron density distribution.

Table 3. Electrostatic valencies at oxygen atoms in borax.

Atoms	Neighbours	Electrostatic valencies	Supposed role in borax
O_1	B_1, B_1	1.50	O_2^-
O_2	B_1, B_2	1.75	O_2^-
O_3	B_1, B_2	1.75	O_2^-
O_4	B_1	0.75	OH^-
O_5	B_2	1.00	OH^-
O_6	Na_1, Na_2	0.33	H_2O
O_7	Na_1, Na_2	0.33	H_2O
O_8	Na_1	0.17	H_2O
O_9	Na_2	0.17	H_2O

The consideration of the electrostatic valencies at the oxygen atoms, however, obviously shows the difference of their parts in the structure, as shown in Table 3. These distribution of electrostatic valencies can best be represented by taking O_1 , O_2 and O_3 (in Table 1 & Table 3) as O^{2-} , O^4 and O^5 as OH^- , and O^6 , O^7 , O^8 and O^9 as H_2O .

On the other hand, among the distances between oxygen atoms where they are not coordinated to the same cation, eleven give the short distances of less than $3.1 \text{ \AA}$ and the rest all greater than $3.3 \text{ \AA}$ which must be classed as van der Waals contacts. These short distances, given in Table 4, may be regarded to suggest the places where the ten hydrogen atoms form hydrogen bonds. From the

Table 4. The distances between oxygen atoms shorter than $3.6 \text{ \AA}$ in borax, excluding those coordinated to the same cation. The distances considered to form hydrogen bonds are shown with stars.

Oxygen-oxygen	Distance ($\text{\AA}$)
O_3-O_5	2.74*
O_1-O_8	2.75*
O_2-O_7	2.82*
O_4-O_6	2.84*
O_4-O_9	2.86*
O_5-O_6	2.86*
O_4-O_7	2.92*
O_8-O_9	2.94*
O_5-O_8	3.11*
O_3-O_9	3.12*
O_4-O_5	3.17
O_1-O_7	3.32
O_2-O_8	3.32
O_4-O_6	3.36
O_2-O_9	3.44
O_3-O_8	3.44
O_2-O_9	3.46
O_4-O_7	3.54
O_6-O_6	3.56

consideration of the tetrahedral or triangular bonds around the oxygen atoms as often observed in many other structures, ten hydrogen atoms were distributed over ten positions out of eleven as given in Table 4. The tetrahedral and triangular arrangements of bonds around the oxygen atoms in borax are shown schematically in Fig. 3, where the probable positions of hydrogen atoms are also drawn.

Fig. 3. The tetrahedral or triangular arrangement of bonds around the oxygen atoms in borax. The probable position of hydrogen atoms are drawn.

This result has certified the identification of atoms arrived at by the electrostatic valencies in the last paragraph.

Description of the structure

The structure of borax is projected on to (100), (010) and (001) in Fig. 4 (a), (b) and (c) respectively. In these figures, the atoms

in only half of the unit cell are shown.

It is clear from the figures that the structure of borax consists of two constituent units, that is, the chains formed by sodium atoms and water molecules, and isolated groups formed by the rest of the constituent atoms. The chains have the composition of $\text{Na}_2 \cdot 8\text{H}_2\text{O}$ and are built up with octahedra of water molecules around Na, which

(a)

Fig. 4. The structure of borax. Numbers give the height of each atom in the cell expressed as a percentage of the a_0 -, b_0 - or c_0 -translation.

- (a) Projection on (100). Only the atoms forming a single sheet are shown.
- (b) Projection on (010). Only the middle half of the unit cell is shown. Broken lines represent the hydrogen bonds holding the isolated group $\text{B}_4\text{O}_5(\text{OH})_4$ to each other.
- (c) Projection on (001). Only the lower half of the unit cell is shown.

(b)

(c)

link each other by holding the $\text{H}_2\text{O}-\text{H}_2\text{O}$ edges in common. These chains are stretched parallel to each other and to the c -axis. The isolated groups are composed of two tetrahedra formed by O^{2-} and OH^- around B_1 and two triangles formed by O^{2-} and OH^- around B_2 by sharing some of O^{2-} so as to make the composition of $\text{B}_4\text{O}_5(\text{OH})_4$.

The isolated groups are placed in between the chains to make a sheet parallel to (100), the attraction between them being due to the hydrogen bonds. In this sheet, moreover, the isolated groups are connected with the neighbouring ones through the hydrogen bonds between O_3 and O_5 ($\text{O}_3 \cdots \text{H}-\text{O}_5$: 2.74 Å), and make a chain parallel to the chains of water molecules around Na. This relation

Table 5. Interatomic distances in borax (in Å).

1. Octahedron around Na_1		2. Octahedron around Na_2	
Na_1-O_6	2.40	Na_2-O_6	2.45
Na_1-O_7	2.44	Na_2-O_7	2.44
Na_1-O_8	2.40	Na_2-O_9	2.40
O_6-O_7	3.39, 3.41	O_6-O_7	3.39, 3.50
O_6-O_8	3.36, 3.40	O_6-O_1	3.17, 3.68
O_7-O_8	3.38, 3.44	O_7-O_9	3.16, 3.16
3. Tetrahedron around B_1		4. Triangle around B_2	
B_1-O_1	1.47	B_2-O_2	1.36
B_1-O_2	1.46	B_2-O_3	1.32
B_1-O_3	1.54	B_2-O_5	1.40
B_1-O_4	1.46	O_2-O_3	2.38
O_1-O_2	2.42	O_2-O_5	2.34
O_1-O_3	2.44	O_3-O_5	2.34
O_1-O_4	2.40		
O_2-O_3	2.43		
O_2-O_4	2.42		
O_3-O_4	2.40		

is clearly shown in Fig. 4 (b), in which the hydrogen bonds connecting the isolated groups are given specially. Therefore, this structure is best expressed by the formula $B_4O_5(OH)_4 \cdot Na_2 8H_2O$. The perfect cleavage parallel to (100) may be explained from this structure, since (100) is the direction of the extension of sheets which are held together mainly by hydrogen bonds.

The interatomic distances in this structure are given in Table 5. It follows from the accuracy of this structure that Na-O distances have a standard error of 0.02 Å, B-O distances of 0.03 Å and O-O distances of 0.03 Å. The octahedron formed by water molecules around Na_1 is a regular one within the limits of error, but those around Na_2 is a little distorted. The mean values of interatomic distances Na-H₂O and H₂O-H₂O are 2.42 Å, and 3.45 Å respectively, in which the distance Na-H₂O is a little larger than the sum of the Goldschmidt radii, 2.30 Å. B_1 is coordinated by four neighbours, one OH⁻ and three O²⁻, arranged at the corners of a regular tetrahedron. The mean interatomic distances B-O(OH) and O-O(OH) are 1.48 Å and 2.42 Å respectively. These tetrahedra are found in datolite⁶⁾ with the interatomic distances B-O(OH) 1.49 Å and O-O(OH) 2.43 Å. B_2 has three neighbours triangularly, one OH⁻ and two O²⁻. The mean values of B-O(OH) and O-O(OH) are 1.36 Å and 2.35 Å respectively, which are comparable with the triangle B(OH)₃ in boric acid¹³⁾, 1.36 Å of B-OH and 2.356 Å of OH-OH.

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