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A Refinement of the Crystal Structure of Danburite*

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The crystal structure of danburite, $CaB_2Si_2O_8$, which was solved by Dunbar & Machatschki (1930), has been refined by the method of least squares. The boron atom is found to be in the center of a BO_4-tetrahedron with no significant differences between the four boron–oxygen distances. The average value of the cation–oxygen distances within the BO_4-tetrahedra is $1\cdot47\pm0\cdot02$ Å and within the SiO_4-tetrahedra $1\cdot62\pm0\cdot01$ Å.

Introduction

Danburite, $CaB_2Si_2O_8$, has been reported to contain a framework of silicon and boron tetrahedra in the form of Si_2O_7 and B_2O_7 pairs (Dunbar & Machatschki, 1930). The positions of the boron atoms within the B_2O_7-groups could not be accurately determined but seemed to be displaced away from the center of the tetrahedron toward the center of one of its sides. With this arrangement, however, the B–O distances seem to be rather unlikely. They would be more plausible if the boron atom were assumed to be close to the center of the tetrahedron (*Strukturbericht*, 1937), but for the bridging oxygen this would lead to a very low value, 1·5, for the sum of the bond strengths. A refinement of the structure is therefore of interest especially as other compounds have been reported to contain the boron atom in an unsymmetrical place in the BO_4-group (Berger, 1953; Ito *et al.*, 1951).

Experimental procedure

As reported by D. & M. danburite is orthorhombic with the space group *Pnma* and has four formula weights per unit cell. The cell dimensions determined in a Straumanis-type powder camera are

$$a = 8\cdot04,\ b = 7\cdot74,\ c = 8\cdot77\ \text{Å}$$
$$(\text{Cu } K\alpha,\ \lambda = 1\cdot5405\ \text{Å})\,.$$

Those previously given by D. & M. are (after transforming the setting from *Pbnm*)

$$a = 8\cdot01,\ b = 7\cdot72,\ c = 8\cdot75\ \text{Å}\,.$$

The differences are probably due to the change in the wave length scale.

Crystals with maximum dimensions less than about 0·2 mm. were photographed with Mo $K\alpha$ radiation in a Weissenberg camera with rotation about the *a*- and *b*-axes. The intensities were estimated visually by comparison with an intensity scale and after correction for Lorentz and polarization factors they were placed on a common scale by use of reflections occurring on both sets of photographs. No corrections for absorption were made (linear absorption coefficient 17 cm.$^{-1}$).

Structure determination

On a rotation photograph around the *b*-axis the $h1l$ reflections were much weaker than the $h0l$ reflections indicating that some of the atoms must be close to the planes $y = 0$ and $y = \frac{1}{2}$. The calcium atoms, however, which must be in fourfold positions, that is, on the mirror planes at $y = \pm\frac{1}{4}$, have a maximal contribution to the $h1l$ reflections and can therefore be expected to appear clearly on a generalized Patterson projection calculated from these reflections. Maxima were found on this projection that could be interpreted as coming from atoms at approximately the positions given by D. & M. for the calcium atoms. The positions of the silicon atoms were also found in the same way. From the parameters for the calcium and silicon atoms most of the signs of the $h1l$ reflections could be determined, and the generalized projection:

$$\varrho_1(xz) = \int_0^1 \varrho(xyz)\sin 2\pi y\, dy = -\sum_h\sum_l F(h1l)\sin 2\pi(hx+lz)$$

was calculated. With the parameters obtained from this projection the signs of the $h0l$ and $h3l$ reflections were determined and the $h0l$ and the generalized $h3l$ projections were calculated. From these all the parameters could be obtained, although the *y* parameter for the boron atom had a relatively large uncertainty. They are compared in Table 1 with those given by D. & M. The largest differences, more than 0·5 Å, occur for the boron atom and for one of the oxygens in four-fold position.

The *x*- and *z*-parameters were now refined by three cycles of least squares with use of 135 observed $h0l$ reflections. Weighting factors were calculated according to the weighting procedure described by Hughes (1941). During the course of the refinement the

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Table 1. *Positional parameters*

		D.&M.	Fourier-projections	*h0l* refinement	*0kl* refinement	Partial 3-dim. refinement
Ca	*x*	$0{\cdot}37_{5}$	0·384	0·3859	—	0·3858
	y	$\frac{1}{4}$	$\frac{1}{4}$	—	$\frac{1}{4}$	$\frac{1}{4}$
	z	$0{\cdot}06_{25}$	0·078	0·0761	0·077	0·0765
Si	*x*	$0{\cdot}05_{8}$	0·055	0·0535	—	0·0535
	y	$0{\cdot}93_{75}$	0·939	—	0·9443	0·9447
	z	$0{\cdot}18_{75}$	0·191	0·1925	0·1923	0·1926
B	*x*	$0{\cdot}31_{25}$	0·253	0·2589	—	0·2597
	y	$0{\cdot}12_{5}$	0·10	—	0·0783	0·0787
	z	$0{\cdot}43_{75}$	0·423	0·4201	0·420	0·4196
$\mathrm{O_{I}}$	*x*	$0{\cdot}20_{0}$	0·197	0·1924	—	0·1931
	y	0	0·000	—	0·9968	0·9964
	z	$0{\cdot}10_{0}$	0·070	0·0676	0·068	0·0680
$\mathrm{O_{II}}$	*x*	$0{\cdot}13_{9}$	0·127	0·1245	—	0·1250
	y	$0{\cdot}97_{2}$	0·970	—	0·9602	0·9590
	z	$0{\cdot}37_{5}$	0·363	0·3658	0·3656	0·3655
$\mathrm{O_{III}}$	*x*	$0{\cdot}41_{7}$	0·393	0·4000	—	0·3996
	y	$0{\cdot}08_{3}$	0·071	—	0·0758	0·0781
	z	$0{\cdot}31_{25}$	0·313	0·3124	0·311	0·3124
$\mathrm{O_{IV}}$	*x*	$0{\cdot}50_{0}$	0·482	0·484	—	0·4863
	y	$\frac{3}{4}$	$\frac{3}{4}$	—	$\frac{3}{4}$	$\frac{3}{4}$
	z	$0{\cdot}31_{25}$	0·328	0·3357	0·3368	0·3365
$\mathrm{O_{V}}$	*x*	$0{\cdot}25_{0}$	0·189	0·1844	—	0·1848
	y	$\frac{1}{4}$	$\frac{1}{4}$	—	$\frac{1}{4}$	$\frac{1}{4}$
	z	$0{\cdot}43_{75}$	0·429	0·4258	$0{\cdot}43_{5}$	0·4272

R-factor, defined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, was reduced from 0·147 to 0·083.

Quite independently the *y*- and *z*-parameters were refined in the same way from 73 *0kl* reflections; the *R*-factor dropping from 0·144 to 0·076 in four cycles. During these refinement cycles the same isotropic temperature factor was used for all the atoms. The scattering curves used were those given by Berghuis *et al.* (1955) for Ca and O, by McWeeny (1951) for B, and by *Internationale Tabellen* for Si. The refined parameters are given in Table 1.

Because of overlap in the *0kl*-projection the *z*-parameter shifts for most of the atoms oscillated between rather large values during consecutive cycles. This was also observed for the *x*-parameter shift for $\mathrm{O_{IV}}$ in the *h0l*-refinement. In order to obtain more accurate parameters a partial three-dimensional refinement was therefore carried out, using 538 observed reflections from the *h0l*, *h1l*, *h2l*, *h3l*, *0kl*, *1kl*, and *2kl* levels, and starting with the parameters obtained in the *h0l*- and *0kl*-refinements. An individual isotropic temperature factor was used for each atom. After three refinement cycles all the indicated parameter shifts were less than 0·0002 and the *R*-value, including only the observed reflections, was 0·095. The temperature factors used in the 3rd refinement cycle were 0·52 Å^2 (Ca), 0·49 Å^2 (Si), 0·57 Å^2 (B), 0·39 Å^2 ($\mathrm{O_{I}}$), 0·51 Å^2 ($\mathrm{O_{II}}$), 0·45 Å^2 ($\mathrm{O_{III}}$), 0·29 Å^2 ($\mathrm{O_{IV}}$) and 0·34 Å^2 ($\mathrm{O_{V}}$). The resulting positional parameters are given in Table 1. Observed and calculated structure factors are compared in Table 2.

Standard deviations in atomic coordinates computed from the results of the 3rd refinement cycle are 0·003 Å for Ca and Si, 0·013 Å for B, and 0·009 Å for O. These values lead to standard deviations of $0{\cdot}01_{0}$ Å for Ca–O and Si–O, $0{\cdot}01_{6}$ Å for B–O and $0{\cdot}01_{3}$ Å for O–O distances.

Discussion of the structure

Projections of the structure along the *b*-axis and the *a*-axis are shown in Figs. 1(*a*), (*b*). The bond lengths are given in Table 3. The structure is built up from $\mathrm{Si_2O_7}$- and $\mathrm{B_2O_7}$-groups, as was also found by D. & M. There is however no significant difference between the B–O distances within a $\mathrm{BO_4}$-tetrahedron, and the oxygen ($\mathrm{O_{V}}$) common to two $\mathrm{BO_4}$-tetrahedra is in close contact with the calcium atom. The calcium atom has 7 oxygen atoms ($\mathrm{O_{V}}$, 2 $\mathrm{O_{I}}$, 2 $\mathrm{O_{II}}$, and 2 $\mathrm{O_{III}}$) at an average distance of 2·46 Å and two other oxygens ($\mathrm{O_{II}}$) at 3·01 Å. The sum of the bond strengths for $\mathrm{O_{V}}$ is therefore about 1·8, but the Ca–$\mathrm{O_{V}}$ distance is significantly shorter than the other Ca–O distances.

If the coordination number for Ca is assumed to be seven the $\mathrm{CaO_7}$-polyhedron and the $\mathrm{BO_4}$-tetrahedron have one common edge ($\mathrm{O_{I}}$–$\mathrm{O_{II}}$) and, as might be expected, the $\mathrm{O_{I}}$–$\mathrm{O_{II}}$ distance is shorter than the other O–O distances within the $\mathrm{BO_4}$-tetrahedron. If the two oxygen atoms at a distance of 3·01 Å are included in the coordination polyhedron around the calcium atom, this has another edge ($\mathrm{O_{II}}$–$\mathrm{O_{V}}$) in common with the $\mathrm{BO_4}$-tetrahedron and also an edge ($\mathrm{O_{II}}$–$\mathrm{O_{III}}$) in common with the $\mathrm{SiO_4}$-tetrahedron. These O–O distances are significantly shorter than the other O–O distances within the $\mathrm{B_2O_7}$- and $\mathrm{Si_2O_7}$-groups. No other distances in these groups differ significantly

Table 2. *Observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right, of l, F_o, and F_c. An asterisk indicates that the value given for F_o is the minimum observable F-value for an unobserved reflection

h=0, k=0

0	-	488
2	23	-19
4	78	-79
6	12	-12
8	104	-110
10	30	28
12	21	22
14	27	27
16	39	33
18	37	-30

h=1, k=0

1	-	0
2	16	15
3	98	-98
4	46	-43
5	123	123
6	37	-37
7	20	-21
8	17	16
9	15	-14
10	21	20
11	29	32
12	9*	4
13	46	-39

h=2, k=0

0	42	32
1	35	-30
2	114	-111
3	9	-4
4	11	8
5	28	27
6	77	74
7	10	-8
8	23	-21
9	16	-18
10	25	26
11	21	-19
12	14	-13
13	19	20
14	19	-21

h=3, k=0

1	54	48
2	22	-22
3	75	-63
4	28	-25
5	9	9
6	45	-42
7	7*	-2
8	38	40
9	8*	-4
10	35	35

h=4, k=0

0	71	-62
1	9	-9
2	11	-10
3	76	76
4	29	28
5	38	38
6	15	15
7	24	-23
8	8*	0
9	14	9
10	9*	2
11	39	-39

h=5, k=0

1	64	60
2	31	-29
3	14	12
4	82	79
5	63	-57
6	22	-22
7	13	-12
8	8*	-6
9	9*	-14
10	13	-12
11	10*	-8
12	32	-23
13	35	33
14	36	28

h=6, k=0

0	43	-36
1	61	-62
2	27	25
3	12	-12
4	7*	-2
5	40	-41
6	9*	-5
7	36	-37
8	24	24
9	70	74
10	26	-27

h=7, k=0

1	44	-40
2	34	-32
3	36	32
4	59	58
5	13	-11
6	22	-22
7	25	28
8	9*	-3
9	9*	4
10	10*	-4
11	15	-11
12	24	-22
13	11*	7
14	34	27
15	24	-23

h=8, k=0

0	7*	0
1	39	-35
2	28	23
3	8*	-1
4	32	-30
5	8*	-4
6	23	-15
7	17	-14
8	26	26
9	29	33
10	19	-15

h=9, k=0

1	30	-28
2	14	15
3	22	21
4	17	16
5	9*	-4
6	12	-11
7	26	22
8	10*	5
9	10*	-1
10	10*	1
11	11*	-5
12	16	-16
13	11*	1
14	12*	3
15	27	-20

h=10, k=0

0	9*	9
1	17	17
2	27	27
3	23	23
4	10*	-10
5	32	26
6	22	-20
7	10*	7
8	10*	-8
9	38	-35
10	18	-16
11	16	-21

h=11, k=0

1	9*	1
2	9*	-2
3	10*	3
4	63	-56
5	15	-11
6	10*	-2
7	21	16
8	17	20
9	11*	-5
10	23	18
11	16	-11
12	19	19
13	11*	-6
14	23	13

h=12, k=0

0	35	-30
1	36	28
2	10*	2
3	17	-16
4	10*	8
5	18	-16
6	11*	4
7	23	20

h=13, k=0

1	11*	16
2	28	21
3	11*	2
4	30	-22
5	30	-23
6	26	24
7	11*	-3
8	11*	-5
9	11*	-1
10	23	-21

h=14, k=0

0	34	-29
1	39	32
2	11*	-9
3	11*	1
4	11*	6
5	12*	-11
6	13	16
7	21	17
8	26	20

h=16, k=0

0	33	28

h=0, k=1

1	-	-11
3	82	-87
5	65	-68
7	21	22
9	30	36
11	26	28

h=1, k=1

1	3*	-1
2	77	64
3	9	-10
4	20	22
5	23	23
6	21	21
7	7*	-3
8	14	-13
9	8*	0
10	27	-31

h=2, k=1

0	94	96
1	51	45
2	4*	-3
3	9	10
4	21	-19
5	8	-8
6	15	-14
7	17	15
8	31	-31
9	15	-13
10	14	13

h=3, k=1

1	53	-50
2	5*	-1
3	29	-29
4	69	-67
5	63	61
6	6*	-4
7	18	19
8	16	21
9	9	7
10	12	12
11	9*	-1
12	14	13
13	32	-32

h=4, k=1

0	54	55
1	45	44
2	5*	-4
3	25	26
4	6*	-1
5	10	12
6	7*	-7
7	12	13
8	27	-28
9	28	-29
10	11	13
11	15	-18

h=5, k=1

1	23	23
2	6*	2
3	15	-14
4	38	-40
5	7*	1
6	7*	-3
7	20	-20
8	19	21
9	8*	-1
10	10	10

h=6, k=1

0	40	-41
1	14	15
2	26	-26
3	13	12
4	18	20
5	7*	-3
6	24	26
7	8*	2
8	9	12
9	9*	-7
10	9*	8
11	10*	-11
12	17	-19

h=7, k=1

1	30	32
2	7*	6
3	7*	6
4	12	11
5	18	-21
6	8*	-3
7	26	-29

h=8, k=1

0	21	-25
1	18	-16
2	8*	-8
3	9	-11
4	8*	9
5	17	-17
6	9*	9
7	9*	-1
8	10*	13
9	29	27

h=9, k=1

1	12	-12
2	8*	6
3	9*	7
4	33	30

h=10, k=1

0	23	22
1	21	-18
2	19	18
3	9*	-7
4	8	-8
5	10*	-9
6	28	-26
7	10*	-6
8	11*	-11
9	22	21

h=11, k=1

1	23	-24
2	10*	3
3	10*	5
4	14	14
5	11*	13
6	11*	-8
7	20	16

h=13, k=1

1	10*	1
2	18	-16
3	11*	5
4	24	-23

h=14, k=1

0	21	-15

h=0, k=2

0	83	95
2	70	-68
4	5*	-1
6	52	50
8	20	-17
10	24	22
12	31	-34

h=1, k=2

1	66	63
2	20	17
3	11	-10
4	9	-10
5	23	24
6	28	-30
7	69	-80
8	8*	-2
9	17	-14
10	9*	5
11	34	37

h=2, k=2

0	-	-9
1	93	-75
2	54	-50
3	75	-70
4	21	20
5	12	-10
6	30	28
7	7*	0
8	12	-11
9	25	24
10	25	26
11	16	15
12	20	-19

h=3, k=2

1	67	-62
2	49	48
3	35	-33
4	64	68
5	42	42
6	19	-18
7	35	38
8	8	-5
9	24	28
10	9*	-11
11	10	-10
12	34	-27
13	37	-33

h=4, k=2

0	10	10
1	42	-40
2	47	44
3	18	17
4	14	13
5	13	13
6	56	-56
7	21	-19
8	33	-34
9	26	26
10	11	14
11	14	-11
12	24	21

h=5, k=2

1	6*	2
2	47	-49
3	21	20
4	47	48
5	17	-19
6	17	-17
7	8	10

h=6, k=2

0	-26	25
1	20	-20
2	31	31
3	48	51
4	7*	2
5	13	12
6	24	-27
7	38	-41
8	14	12
9	21	16
10	14	-11
11	22	-19

h=7; k=2

1	23	-28
2	75	-86
3	33	37
4	8*	-13
5	21	-20
6	28	-30
7	9*	5
8	19	20
9	10*	9
10	37	43

h=8, k=2

0	41	-45
1	16	-13
2	8*	4
3	24	25
4	9*	-6
5	18	21
6	9*	7
7	20	-18
8	48	43

h=9, k=2

1	9*	5
2	21	21
3	27	31
4	36	35
5	39	-32

h=10, k=2

0	28	-31
1	13*	-14
2	13*	1
3	28	-23

h=11, k=2

1	13*	8
2	19	19
3	15	11
4	13*	-3
5	18	-19

h=12, k=2

0	22	-10
1	13*	4
2	15	14
3	28	-28

h=13, k=2

1	18	-25

h=14, k=2

1	24	23

h=0, k=3

1	49	50
3	50	52
5	24	27
7	7*	1
9	33	-33

h=1, k=3

1	35	39
2	65	-61
3	19	-21
4	44	-46
5	11	14
6	25	26
7	41	-44
8	8*	-5
9	13	-12
10	11	16
11	29	31
12	29	25
13	11*	4
14	19	-17

h=2, k=3

0	85	74
1	21	22
2	77	-74
3	9	-9
4	6*	-6
5	11	9
6	60	60
7	10	8
7	11	-13
9	32	-31
10	15	16
11	13	14
12	22	-23
13	12*	-2
14	16	-16

h=3, k=3

1	42	46
2	59	62
3	50	-52
4	6*	6
5	47	50
6	20	23
7	40	-49
8	19	-23
9	15	19
10	17	-19
11	36	35
12	11*	5
13	14	-12

h=4, k=3

0	40	42
1	17	-20
2	63	-69
3	64	-74
4	8	11
5	14	-16
6	45	53
7	23	26
8	26	-26
9	9*	4
10	23	26
11	31	33
12	13*	-15
13	13*	5
14	16	-19

h=5, k=3

1	27	28
2	29	32
3	51	-53
4	7*	7
5	33	35
6	9*	6
7	10*	-11
8	11*	-12
9	11*	-3
10	15	-11
11	13	12
12	13*	1
13	17	-14

h=6, k=3

0	54	61
1	7*	-7
2	8*	3
3	9	8
4	8*	1
5	9*	9
6	17	-22
7	9*	-7
8	44	-49
9	10*	-2
10	22	17
11	11*	0
12	14	20

h=7, k=3

1	25	-29
2	30	-31
3	23	-25
4	23	24
5	35	38
6	8	-9
7	27	36

h=8, k=3

0	15	16
1	25	-28
2	9*	2
3	25	26
4	9*	-4
5	10*	8
6	10*	-6
7	25	-29
8	11*	-7
9	21	23

h=9, k=3

1	10*	12
2	56	-58
3	10*	6
4	19	19
5	11*	-10
6	28	-25
7	13	-15
8	12*	13
9	12*	-7
10	27	29

h=10, k=3

0	10*	-11
1	24	-26
2	10*	-10
3	39	40
4	11*	-6
5	27	28
6	11	20
7	35	-32
8	12	20
9	12*	6
10	12*	-8
11	26	-23

h=11, k=3

1	11*	10
2	13	-15
3	11*	5
4	29	26
5	12*	-9
6	30	-23

h=12, k=3

0	19	-13
1	34	-29

h=0, k=4

0	127	133
2	44	46
4	36	-38
6	38	-41
8	37	-38
10	13*	-12
12	21	22
14	31	30

h=0, k=5

1	41	43
3	59	-61
5	65	-65
7	33	35
9	17	20
11	34	35
13	16*	-7
15	24	-19

h=0, k=6

0	92	-98
2	21	21
4	18	18
6	12*	1
8	47	50
10	24	-24
12	23	-23

h=0, k=7

1	58	61
3	36	38
5	15	15
7	13*	5
9	40	-40

h=0, k=8

0	12*	-4
2	56	61
4	13*	-12
6	47	-52
8	14*	-3
10	34	-29
12	30	30
14	25	26

h=0, k=9

1	14*	17
3	17	-18
5	27	-31
7	15*	14
9	23	12

h=0, k=10

0	53	-58
2	14	16
4	17	15
6	15*	-6
8	28	20

h=0, k=11

1	15*	6
3	34	39
5	25	24
7	20	-14

h=0, k=12

0	29	34
2	20	24
4	16*	-7
6	36	-30
8	33	-34
10	17*	-2
12	36	29

h=0, k=13

1	24	-23

h=1, k=4

1	24	-27
2	33	-36
3	7	-9
4	33	-36
5	28	30
6	21	-25
7	18	17
8	19	19
9	9*	2
10	28	29

h=1, k=5

1	6*	-5
2	43	49
3	8	-10
4	14	-13
5	30	31
6	45	47
7	19	-18
8	21	-20
9	9*	-4
10	34	-39
11	12	15
12	13	8

h=1, k=6

1	10	13
2	15	-18
3	45	53
4	12	-13
5	49	-58
6	8*	-9
7	14	-17

h=1, k=7

1	7*	5
2	15	-20
3	8*	5
4	38	-42
5	8*	4
6	24	25
7	18	-20
8	9*	-3
9	10*	-5
10	10*	7
11	12*	12
12	29	25

h=1, k=8

1	21	-26
2	21	-27
3	23	25
4	29	-33
5	22	-23
6	9*	-1
7	39	41
8	10*	10
9	10*	4
10	16	17
11	31	-27

h=1, k=9

1	19	-22
2	20	26
3	9*	12
4	9*	7
5	11	9
6	11*	17
7	11*	9
8	12*	-8
9	12*	3
10	29	-29

h=1, k=10

1	11*	14
2	10*	1
3	21	26
4	10*	-8
5	37	-41

h=1, k=11

1	12*	0
2	20	-25

h=2, k=4

0	5*	-2
1	17	-21
2	25	-26
3	11	11
4	6*	-5
5	17	17
6	18	22
7	14	-13

h=2, k=5

0	116	108
1	56	53
2	21	-21
3	10	-9
4	25	-25
5	10	-11
6	6*	2
7	28	27
8	34	-35
9	28	-27
10	18	18

h=2, k=6

0	33	-39
1	21	-25
2	22	22
3	37	-39
4	8*	0
5	20	-20
6	22	-21
7	9*	0
8	22	21
9	23	23
10	11*	-2
11	25	22

h=2, k=7

0	8*	11
1	9	12
2	25	-25
3	19	-19
4	8*	-6
5	8*	-3
6	29	30
7	13	10
8	12	13
9	11*	-11
10	11*	-2
11	18	16
12	20	-20

h=2, k=8

0	26	-31
1	23	24
2	16	15
3	9*	8
4	9*	-9
5	10*	-3
6	10*	-5
7	10*	0
8	30	25
9	20	-12

h=2, k=9

0	11	17
1	9*	5
2	13	19
3	11*	-11
4	17	-14
5	12*	-12
6	30	-22

h=2, k=10

0	30	-37
1	12*	13
2	12*	12
3	24	-27
4	12*	3
5	34	-27
6	12*	-7
7	12*	11
8	26	22

h=2, k=11

0	21	-28
1	16	-18

h=2, k=12

0	14*	-15
1	19	26

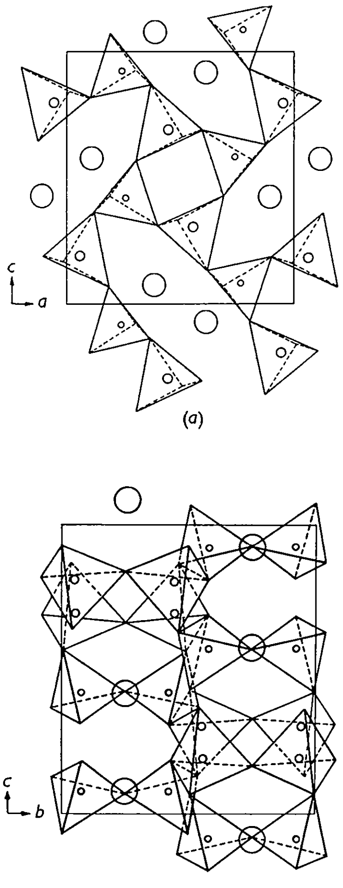
Table 3. *Bond lengths*

Within a B_2O_7-group	
B–O_{V}	1·46
–O_{I}	1·47
–O_{II}	1·50
–O_{III}	1·47
O_{I}–O_{II}	2·33*
–O_{III}	2·43
–O_{V}	2·47
O_{II}–O_{III}	2·44
–O_{V}	2·36*
O_{III}–O_{V}	2·40

Within a Si_2O_7-group	
Si–O_{IV}	$1{\cdot}62_1$
–O_{I}	$1{\cdot}61_7$
–O_{II}	$1{\cdot}62_5$
–O_{III}	$1{\cdot}61_2$
O_{I}–O_{II}	2·68
–O_{III}	2·66
–O_{IV}	$2{\cdot}66_5$
O_{II}–O_{III}	2·56*
–O_{IV}	$2{\cdot}64_5$
O_{III}–O_{IV}	2·64

Within a CaO_9-group	
Ca–O_{V}	$2{\cdot}40_5$
–2 O_{I}	$2{\cdot}50_2$
–2 O_{II}	$2{\cdot}45_8$
–2 O_{III}	$2{\cdot}46_1$
–2 O_{II}	$3{\cdot}00_5$
O_{I}–O_{I}	3·92
–O_{II}	2·33, 3·53
–O_{III}	2·78
O_{II}–O_{II}	3·16, 3·23
–O_{III}	2·56, 3·93
–O_{V}	2·36, 3·48
O_{III}–O_{III}	2·66
–O_{V}	3·38

* Common with the coordination polyhedron of Ca.



(*a*)

(*b*)

Fig. 1*. (*a*) Projection of the structure along the *b*-axis. (*b*) Projection of the structure along the *a*-axis. Large circles represent calcium atoms. The smaller circles represent boron atoms. Oxygen atoms are at all the vertices of the tetrahedral figures.

from their average values with the possible exception of the O–O distances in the BO_4-tetrahedron, which show somewhat larger deviations.

The average value of the B–O distances is $1{\cdot}47_5$ Å. Schulze (1934) has reported the B–O distances for tetrahedrally coordinated boron to be 1·49 Å in $BAsO_4$ and 1·44 Å in BPO_4. Zachariasen (1937) has found the distance 1·53 Å in $KH_2(H_3O)_2B_5O_{10}$, and 1·42–1·51 Å in a preliminary report on the structure of HBO_2 (1952). Ito *et al.* (1951) have found 1·48 Å in boracite, $ClMg_3B_7O_{13}$; Collin (1951) 1·42 Å in bandylite, $CuCl_2.CuB_2O_4.4\,H_2O$; Fornaseri (1949) 1·41 Å in teepleite, $NaBO_2.NaCl.2\,H_2O$; and Clark & Christ (1957) $1{\cdot}4_7$ Å in $CaB_3O_3(OH)_5.2\,H_2O$.

In the Si_2O_7-group the average Si–O distance is 1·62 Å which is somewhat larger than the value 1·60±0·01 Å accepted by Smith (1954). The average O–O distance, excluding the short O_{II}–O_{III} distance, is 2·66 Å.

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* 'The dotted and the full lines which indicate the farther and nearer edges of the pairs of tetrahedra at the lower right hand corner and at the upper left hand corner of Fig. 1(b) have been interchanged'.