Structure of Danburite, $CaB_2Si_2O_8$.

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(With 6 Figures.)

Danburite is a silicate of calcium and boron whose chemical composition can be represented by the formula $CaB_2Si_2O_8$. It belongs to the ortho-rhombic class of crystals and its structure affords another example of a silicate in which each silicon atom is surrounded by four oxygen atoms. Although the ratio of the oxygen to silicon atoms in the unit cell is four to one, the unit of the structure is not a silicon tetrahedron but an Si_2O_7 group, two tetrahedral groups being linked together by a common oxygen atom which lies on a reflexion plane. This accounts for seven of the eight oxygen atoms in the chemical formula. It will be shown that the eighth oxygen atom is placed on a reflexion plane in such a way as to form a tetrahedron with oxygen atoms from three Si_2O_7 groups, and into these tetrahedra the boron atoms have been placed. Thus we have in the structure, not only a series of Si_2O_7 groups, but also B_2O_7 groups.

Although the presence of the boron atoms has added to the attractiveness of the problem, it has also increased the difficulties of solution. The normal scattering power of the boron atoms is so small that it is not easy to assign definite parameters to their position purely from consideration of the experimental F values, and it must be admitted that the parameters given in the final structure were derived mainly from physical considerations. Since no F curve for this atom was available, we have tried to make an approximate allowance by assuming that as far as their scattering power is concerned, the eight boron atoms in the unit cell are equivalent to three oxygen atoms.

Unit Cell and Space Group.

The unit cell, which contains four molecules of $CaB_2Si_2O_8$ has dimensions

$$a = 8.75\ \text{Å};\ b = 8.01\ \text{Å};\ c = 7.72\ \text{Å};$$

giving the axial ratios

$$a : b : c = 1 : 0.9154 : 0.8822.$$

The crystal used for our investigation was kindly supplied to us by W. Zachariasen of the University of Oslo. The space group was determined by W. Jackson (Manchester) from an analysis of six rotation photographs taken about the three rectangular axes in turn as axes of rotation. The results have been checked by observations taken with an ionisation spectrometer. It was found that the reflexions satisfy the following conditions:

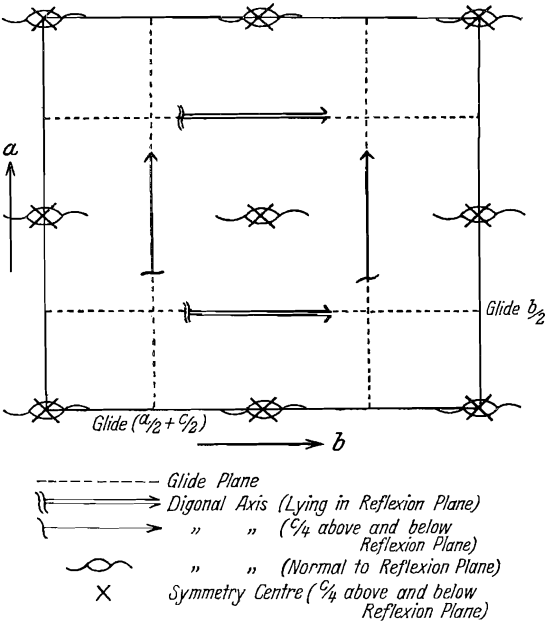

Fig. 1. Symmetry elements of the space group V_h^{16}.

Indices (hkl) — all types present
Indices $(hk0)$ — all types present
Indices $(h0l)$ — $(h + l)$ even
Indices $(0kl)$ — k even.

These results are consistent with either of the space groups V_h^{16} or C_{2v}^{9}, between which X-ray data alone cannot distinguish. As there was no definite reason for supposing that the crystal did not possess holohedral symmetry, V_h^{16} was adopted as the true space group, and nothing has arisen during the solution of the structure to suggest that this assumption was incorrect.

The symmetry elements of V_h^{16} projected on to a reflexion plane are shown in Fig. 1. Taking a symmetry centre at the centre of the unit cell as origin, the elements of symmetry have the following positions:

Reflexion planes $(0\ 0\ 1)_{\frac{1}{4}}$, $(0\ 0\ 1)_{-\frac{1}{4}}$
Glide planes $(0\ 1\ 0)_{\frac{1}{4}}$, $(0\ 1\ 0)_{-\frac{1}{4}}$; translation $(a/2 + c/2)$
Glide planes $(1\ 0\ 0)_{\frac{1}{4}}$, $(1\ 0\ 0)_{-\frac{1}{4}}$, translation $b/2$
Symmetry centres $(0\ 0\ 0)$, $(0\ 0\ \frac{1}{2})$, $(\frac{1}{2}\ \frac{1}{2}\ 0)$, $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$;
$(\frac{1}{2}\ 0\ 0)$, $(\frac{1}{2}\ 0\ \frac{1}{2})$, $(0\ \frac{1}{2}\ 0)$, $(0\ \frac{1}{2}\ \frac{1}{2})$.

An atom in the general position (x, y, z) in the unit cell is converted by the operation of the symmetry elements into eight atoms within the cell. If

$$\theta_1 = \frac{2\pi x}{a}; \qquad \theta_2 = \frac{2\pi y}{b}; \qquad \theta_3 = \frac{2\pi z}{c};$$

the equivalent positions are

$$\pm[\theta_1, \theta_2, \theta_3]; \qquad \pm[(\theta_1 - \pi), (\pi - \theta_2), (\theta_3 - \pi)]$$
$$\pm[\theta_1, \theta_2, (\pi - \theta_3)]; \quad \pm[(\theta_1 - \pi), (\pi - \theta_2), -\theta_3].$$

The resultant scattering power of the eight equivalent atoms is

$$F'_{(hkl)} = F_a \sum \cos(h\theta_1 + k\theta_2 + l\theta_3) \qquad (1)$$

where F_a is the atomic scattering power for reflexion in the plane (hkl). The above equation reduces to

$$F'_{(hkl)} = 8\,F_a \cos[h\theta_1 + (h+k)\pi/2] \cos[k\theta_2 + (h+k+l)\pi/2] \cos[l\theta_3 + l\pi/2].$$

The structure amplitude for the whole cell is given by

$$F_{(hkl)} = \sum F'_{(hkl)}$$

the summation extending over all the sets of equivalent atoms in the cell. From equation (1) can be deduced the reflexions which may occur in accordance with the space group, and also the corresponding phase factor. In cases when an atom lies at a symmetry centre or on a reflexion plane, the number of equivalent positions reduces to four.

Experimental Methods.

A detailed account of the general methods employed in obtaining the experimental F values for a large number of atomic planes is given in the paper "A technique for the X-ray examination of crystal structures with many parameters" [1]) by W. Lawrence Bragg and J. West.

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[1]) W. Lawrence Bragg and J. West, Z. Krist. **69**, Parts 1/2, 118. 1928.

The symbols there adopted will be used in this paper without further definition.

Only the two faces (001) and (110) occurred naturally on the crystal from which our reflexions were obtained. The (100) and (010) faces were ground on the crystal and the series of integrated intensities measured from these faces, supplemented by the use of crystal sections cut perpendicular to the 'a' and 'c' axes. Unfortunately, the crystal was not sufficiently large to provide a third section cut perpendicular to the 'b' axis, so that no quantitative estimates of the integrated intensities for planes of the type ($h0l$) are available.

The use of crystal sections enables one to determine rapidly the value of the integrated reflexion for a large number of planes in the same zone[1]. The section is mounted in a circular holder on a spectrometer table in such a way that any desired set of planes can be brought into the reflecting position. A simple calculation gives the appropriate position of the ionisation chamber. The absolute intensity of reflexion of these planes is obtained by comparing the relative intensity measured in the above way with the relative intensity of another spectrum in this zone whose absolute intensity has previously been measured from a face. It is possible, therefore, to reduce all slip reflexions to absolute intensities from a face. It is desirable that, before being used, the section should be ground down to its optimum thickness in order that the reflexions may not be reduced in intensity to too great a degree.

Since

$$\varrho = Qe^{-\mu t}$$

the optimum thickness is $1/\mu$, where μ is the absorption coefficient of the crystal for X-rays.

If reflexion is obtained from the extended face of a mosaic crystal[2])

$$\varrho = \frac{N^2 e^4 \lambda^3}{4\mu m^2 c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot F^2 = \frac{Q}{2\mu} \qquad (2)$$

or

$$= A\Theta F^2$$

where $A = \dfrac{N^2 e^4 \lambda^3}{4\mu m^2 c^4}$ and $\Theta = \dfrac{1+\cos^2 2\theta}{\sin 2\theta}$.

Since the unit cell has dimensions

$$a = 8.75\,\text{Å}; \quad b = 8.01\,\text{Å}; \quad c = 7.72\,\text{Å}$$

and the number of unit cells per c.c. is given by $1/a \cdot b \cdot c$

$$N^2 = 3.417 \times 10^{42}.$$

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1) W. Lawrence Bragg and J. West, Z. Krist. **69**, Parts 1/2, 118. 1928.

2) C. G. Darwin, Phil. Mag. **27**, 315. 1914; **27**, 675. 1914; **43**, 800. 1922; A. H. Compton, Phys. Rev. **9**. 29. (January 1917); P. P. Ewald, Phys. Z. **26**, 29. 1925.

Table 1.

$\lambda = 0.614$ Å.

Indices	$\sin\theta$	Θ	ϱ'	F uncorrected for extinction	$\varrho = \frac{\varrho'}{1 - 2g\varrho'}$	F corrected for extinction	F calculated from structure
200	0.070	15.9	6.7	17	7.2	18	18
400	0.140	6.9	38.5	62	66.9	82	77
600	0.210	4.5	0.8	11	0.8	11	5
800	0.280	3.2	30.5	81	45.9	100	101
1000	0.350	2.4	2.5	27	2.6	27	24
1600	0.561	1.2	2.3	36	2.4	37	34
020	0.076	14.4	10.8	23	12.3	24	19
040	0.153	6.3	19.0	45	24.0	51	47
060	0.229	4.0	4.5	29	4.7	29	31
080	0.306	2.9	Trace	Trace	Trace	Trace	9
0100	0.382	2.1	0	0	0	0	19
0160	0.611	1.1	1.0	25	1.0	25	27
002	0.080	13.2	30.9	40	46.8	50	79
004	0.159	6.1	54.8	79	138	124	116
006	0.239	3.9	27.3	70	39.0	83	86
008	0.319	2.7	0.7	14	0.7	14	9
0010	0.399	2.0	8.0	52	8.8	55	45
0016	0.638	1.1	1.8	34	1.84	34	30
110	0.052	20.0	0	0	0	0	19
120	0.084	12.0	13.2	28	15.4	30	35
130	0.119	8.2	17.0	37	20.9	42	41
140	0.157	6.1	1.0	11	1.0	11	10
150	0.195	4.9	14.8	47	17.7	50	56
210	0.076	14.5	Trace	Trace	Trace	Trace	7
220	0.104	9.4	41.4	55	76.0	75	119
230	0.135	7.2	6.2	24	6.7	25	21
240	0.168	5.7	2.4	17	2.5	17	22
250	0.204	4.7	6.0	30	6.4	31	27
310	0.112	9.1	42.6	57	80.5	78	119
320	0.130	7.6	1.4	11	1.4	11	11
330	0.155	6.3	21.3	48	28.5	56	53
340	0.186	5.1	24.0	56	32.6	66	41
350	0.218	4.2	2.0	18	2.0	18	21
410	0.146	6.6	10.6	32	12.0	35	16
420	0.153	6.3	Trace	Trace	Trace	Trace	25
430	0.181	5.3	6.1	2.8	6.5	29	17
440	0.207	4.5	3.7	24	3.9	24	18
450	0.238	3.9	19.7	59	24.0	65	73
510	0.180	5.3	29.3	62	43.2	75	108
550	0.259	3.5	12.7	50	14.8	54	55

Table 1 (continued).

Indices	$\sin\theta$	Θ	ϱ'	F uncorrected for extinction	$\varrho = \frac{\varrho'}{1-2g\varrho'}$	F corrected for extinction	F calculated from structure
021	0.086	11.5	53.0	57	127	88	130
022	0.112	9.0	1.7	12	1.7	12	4
023	0.142	6.9	36.6	60	61.4	78	63
024	0.177	3.4	Trace	Trace	Trace	Trace	24
025	0.213	4.5	38.8	78	68.0	102	102
026	0.251	3.7	9.1	41	10.1	43	51
041	0.158	6.1	18.5	46	23.2	50	33
042	0.173	5.6	1.2	12	1.2	12	16
043	0.194	4.9	12.5	43	14.5	45	65
044	0.221	4.2	8.5	37	9.4	39	45
045	0.251	3.7	22.5	65	29.9	74	59
061	0.233	4.0	8.5	38	9.4	40	21
062	0.243	3.8	4.0	27	4.2	27	18
063	0.259	3.6	18.0	59	22.5	65	67
064	0.280	3.2	2.6	23	2.7	24	16
065	0.304	2.9	0.7	13	0.7	13	10
066	0.332	2.6	5.4	37	5.7	39	36

The normal linear absorption coefficient, calculated from tables of atomic absorption coefficients, is 10.7

$$\frac{e^2}{mc^2} = 2.816 \times 10^{-13}$$

and

$$A = 1.466 \times 10^{-9}.$$

Since no crystal conforms to the ideally imperfect type, the F values calculated from equation (2) must be corrected for extinction. If ϱ' is the value to which ϱ is reduced as a result of extinction

$$\varrho' = \frac{Q}{2(\mu + gQ)} = \frac{\varrho}{1 + 2g\varrho}$$

or

$$\varrho = \frac{\varrho'}{1 - 2g\varrho'}.$$

In the case of Danburite, the $(00l)$ planes provided a means of determining the extinction factor $2g$. An arrangement in the 'c' direction which would satisfy those experimental F values which were sufficiently small to be almost unaffected by any extinction correction was comparatively easy to determine, and by comparing the larger F values obtained from this arrangement with the values measured experimentally, the extinction factor was estimated to be 1.1×10^4. All other spectra were then corrected using this value.

The experimental F values corrected for extinction are given in Table 1, column 7, and we have now to determine a structure which will give structure amplitudes $F_{(hkl)}$ corresponding as closely as possible to these values.

Deductions from Space Group.

The unit cell contains four calcium atoms, eight boron atoms, eight silicon atoms and thirty-two oxygen atoms. It follows that

a) the calcium atoms must lie in a special position (i. e. either on reflexion planes or at symmetry centres),
b) the boron (and silicon) atoms may consist of a set of eight in the general position or two sets of four in the special positions,
c) the oxygen atoms may consist of n sets of eight in the general position, together with $2(4-n)$ sets of four in the special positions. n can have any one of the values one, two, three or four.

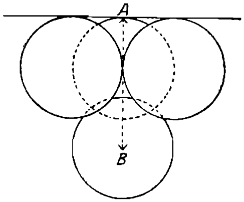

Fig. 2. SiO_4 tetrahedron.

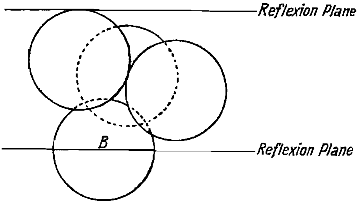

Fig. 3. Probable position of a SiO_4 tetrahedron relatively to the symmetry planes of the structure.

If each silicon atom is surrounded by four oxygen atoms in tetrahedral form then the silicon atoms cannot lie at symmetry centres. If the silicon atoms lie on the reflexion planes, then since the calcium atoms must also lie in a special position, alternate or all 'c' spectra would be normal for calcium and silicon, according to which special position we assign to the calciums. This is certainly not the case, and hence the silicon atoms must lie in the general position.

The volume per oxygen atom in the unit cell is 16.9, so that the structure is fairly close packed. We may assume that the diameter of an oxygen atom is approximately 2.7 Å. Not more than ten oxygen atoms can lie on any one reflexion plane, so that at least one set of eight oxygen atoms must lie in the general position. The distance between the reflexion planes is 3.86 Å. If we consider a silicon tetrahedron (Fig. 2) the distance AB is 3.65 Å.

The basal atoms of the tetrahedron are hardly likely to be on the reflexion plane, since this would mean two silicon tetrahedra sharing a common base and the distance apart of the silicon atoms across the reflexion plane being less than 1 Å. It is more reasonable that the oxygen *B* should lie on one reflexion plane, and the basal atoms almost touch the other plane. One could imagine the requisite distance of 3.86 Å being derived by tilting the tetrahedron over (Fig. 3) until at least one of the base atoms is touching the reflexion plane. The oxygen atoms would therefore consist of three sets of eight in the general position and two sets of four in special positions.

Summarizing, we have:

4 calcium atoms at a special position involving 2 parameters,
24 oxygen atoms in the general position involving 9 parameters,
8 oxygen atoms in special positions involving 4 parameters,
8 silicon atoms in the general position involving 3 parameters.

If we accept for the moment the presence of B_2O_7 groups in the structure, then the boron atoms must lie in the general position, involving another three parameters. The solution of the structure thus requires the evaluation of twenty-one parameters.

Analysis in detail.

Although the structure has approximately the same number of parameters in each of the axial directions, the presence of the reflexion planes perpendicular to the '*c*' axis makes the evaluation of the parameters in the '*c*' direction less complicated.

'*c*' parameters.

If we accept the oxygen arrangement given in Fig. 3, then the silicon parameter must be approximately 22½°. Since the distance of the centre of an oxygen atom from a reflexion plane which the atom touches is the equivalent of 60°, the parameters of the oxygen atoms forming the base of the tetrahedron must be between 0° and 30°.

An analysis of the (0 0 *l*) spectra which occur at a sufficiently large angle for the oxygen contribution to these spectra to be negligible, gives the possible parameters

$$\left.\begin{matrix} Ca\ 0^\circ \\ Si\ 67\tfrac{1}{2}^\circ \end{matrix}\right\} \quad \text{or} \quad \left.\begin{matrix} Ca\ 90^\circ \\ Si\ 22\tfrac{1}{2}^\circ \end{matrix}\right\}.$$

If the silicon parameter is 67½°, the distance apart of two silicon atoms across the reflexion plane would be 0.96 Å. This case can be ruled out without further consideration, and we are left with the second set of parameters for calcium and silicon.

The parameters which were finally adopted (leaving the boron atoms out of account for the moment) are

4 Ca at 90°
8 Si at $22\frac{1}{2}$°
8 O_1 at 0°
8 O_2 at 10°
8 O_3 at 30°
4 O_4 at 90°
4 O_5 at 90°.

As stated previously, the estimation of the extinction factor was based on the above values.

'*a*' and '*b*' parameters.

In order to simplify the determination of these parameters, we will consider the projection of the structure on one of the reflexion planes. It has previously been found from consideration of the $(0\,0\,l)$ spectra that there are layers of oxygen atoms parallel to the reflexion planes which contain the centres of symmetry. It follows that in this projection we may draw circles of diameter 2.5 Å (assuming a lower limit for the radius of the oxygen atom) about the centres of symmetry, and no oxygen atom may have its centre inside one of these circles. For the purpose of determining possible parameters, it is a sufficient approximation to take the projection of the base of the silicon tetrahedron on to this plane as an equilateral triangle of side 2.5 Å, or, in other words, to neglect the inclination of the base of the tetrahedron to the reflexion plane as found from the $(0\,0\,l)$ spectra.

It should be noted that the axis of the unit cell may be written

$$a = 8.75\ \text{Å} \bumpeq 4 \times 2.2\ \text{Å},$$
$$b = 8.01\ \text{Å} \bumpeq 3 \times 2.7\ \text{Å}.$$

This fact suggests that the projection of the basal atoms of the tetrahedron will be such that a median of the equilateral triangle will be approximately parallel to the '*a*' axis.

From consideration of this projection, upper and lower limits can be assigned to the parameters of the oxygen atoms and regions mapped out in which the silicon atoms may lie. For a more detailed account of the methods used, the reader is referred to the paper "The Structure of Diopside" by B. Warren and W. L. Bragg[1]).

This method of finding possible parameters from atomic dimensions may seem a little arbitrary, but no danger is involved in employing the device, since the approximate structure arrived at will certainly not satisfy the experimental F values, even after its adjustment, if fundamentally incorrect.

The more accurate parameters are found from the spectra in the $(h\,0\,0)$ and $(0\,k\,0)$ series and in the $(h\,k\,0)$ zone. A check on the struc-

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[1]) B. Warren and W. Lawrence Bragg, Z. Krist. **69**, Parts 1/2, 168. 1928

ture is given by combining the ‘*a*’ and ‘*b*’ parameters in turn with the ‘*c*’ parameters for spectra in the $(h\,0\,l)$ and $(0\,k\,l)$ zones. The parameters determined in this way are

Table 2.

Atom	*a*	*b*	*c*
4 *Ca*	157½°	— 45°	90°
8 *Si*	67½	21	— 22½
8 O_1	36	72	0
8 O_2	135	50	— 10
8 O_3	67½	— 30	30
4 O_4	67½	0	— 90
4 O_5	— 22½	90	± 90

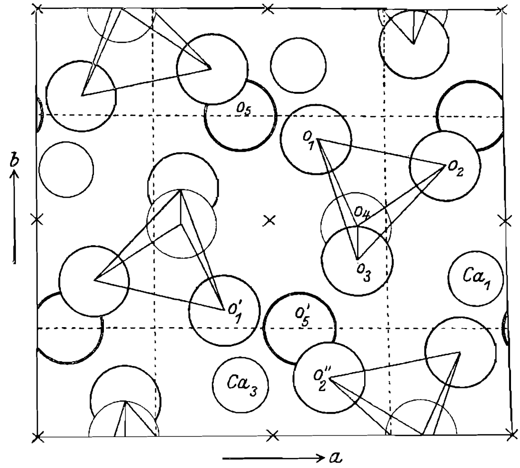

Fig. 4. Projection of the structure on a reflexion plane.

An alternative sign has been given to the ‘*c*’ parameter of O_5. This is due to the fact that the contribution of this atom to spectra in the $(0\,k\,l)$ zone is zero when the phase factor is the product of two sine terms (l odd) and is independent of the sign of the parameter when the phase factor involves two cosine terms (l even). As no quantitative estimate of the scattering power of planes in the $(h\,0\,l)$ zone is available (and even if it were, the contribution of O_5 to these planes is not sufficiently large for one to fix conclusively the sign of the parameter) we may be on safer ground in attempting to fix the sign of the parameter from physical considerations.

A projection of the atomic arrangement on to a reflexion plane is given in Fig. 4. The lightly drawn atoms are the O_4 oxygens which have been definitely fixed in position. It is apparent from the diagram on which reflexion plane each of these atoms lies. The heavily drawn atoms are the O_5 oxygens, the sign of their ‘c’ parameter being at present indefinite.

No matter what this sign may be, each of the O_5 atoms is in such a position by virtue of its ‘a’ and ‘b’ parameters to form a tetrahedron with oxygen atoms from three distinct Si_2O_7 groups. A tetrahedron formed in this way could reasonably contain a boron atom, and the probability of this being the case is enhanced by the fact that the (a, b) parameters of the boron atoms which seem to fit the experimental F values best are $(-22\frac{1}{2}^\circ, 67\frac{1}{2}^\circ)$. The calcium atoms in Fig. 4 are shown as smaller circles.

If the O_5 atoms have the parameters

a	b	c
$-22\frac{1}{2}^\circ$	90°	$+90^\circ$

then the atoms O_4, O_5', Ca_3 all lie on the same reflexion plane. If the allotted numerical parameters are correct, this becomes an impossibility since the distance $O_4\ O_5'$ is less than 2 Å. It can, however, be argued that one might be able to adjust the oxygen parameters so that the experimental F values are still satisfied by the modified structure, and that this structure might also give the requisite distance of approximately 2.7 Å between O_4 and O_5'. Even if this were the case, the structure would not appear probable from a physical point of view owing to the small distance 1.86 Å between O_5' and Ca_3. The distance apart of an oxygen and calcium atom should be of the order of 2.3 Å. No such difficulties exist if O_5 is given the parameters

a	b	c
$-22\frac{1}{2}^\circ$	90°	-90°

The twenty-four parameters determining the structure are therefore taken to be as follows:

Table 3.

Atom	a	b	c
4 Ca	$157\frac{1}{2}^\circ$	-45°	90°
8 Si	$67\frac{1}{2}$	21	$-22\frac{1}{2}$
8 O_1	36	72	0
8 O_2	135	50	-10
8 O_3	$67\frac{1}{2}$	-30	30
4 O_4	$67\frac{1}{2}$	0	-90
4 O_5	$-22\frac{1}{2}$	90	-90
8 B	$-22\frac{1}{2}$	$67\frac{1}{2}$	-45

Comparison of calculated and observed values of $F_{(hkl)}$.

Calculated and observed values of $F_{(khl)}$ are given in Table 1. The general agreement is quite good, and shows that the atomic parameters as determined above cannot be very far wrong. The main discrepancies occur when the F values are large, and this is most probably due to the difficulty experienced in fixing the exact value of the extinction coefficient, rather than to any inaccuracies of the experimental methods. It may be that very slight adjustments of the atomic parameters together with a modification of the extinction coefficient would result in a more exact agreement between calculated and experimental F values, but as the form of the structure is more important than the allotting of extremely accurate parameters to the atoms, it has not been thought necessary to do this.

Discussion of the Structure.

One of the most interesting points of the structure is the presence of the Si_2O_7 groups, although the ratio of silicon to oxygen atoms in the unit cell is 1 : 4. The shape of the group is distorted a little, the distances of the oxygens O_1, O_2, O_3, O_4 from one another being

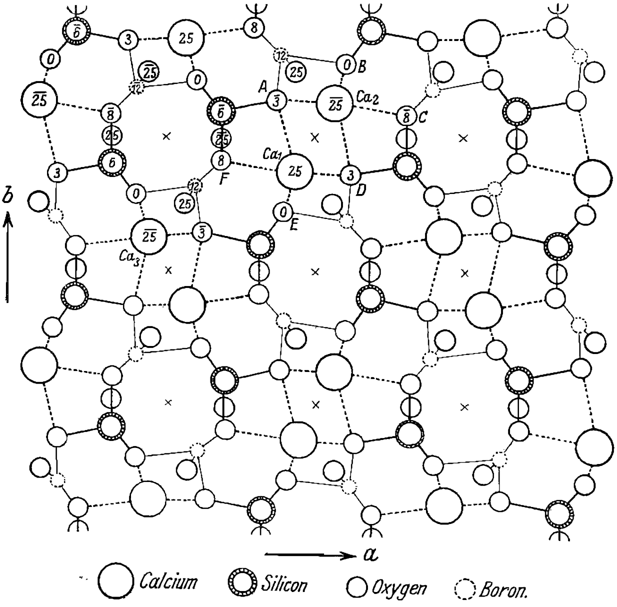

Fig. 5. Projection of the Danburite structure on (001).

2.49 Å, 2.51 Å, 2.48 Å, 2.57 Å, 2.63 Å and 2.66 Å. The result of this distortion, as pointed out previously, is to give a 'c' axis which is larger than one would expect from the diameter of the oxygen atom.

In Fig. 5 is given the projection of the complete structure on to the $(0\,0\,l)$ plane through the origin of co-ordinates. The linkage between an oxygen atom and a silicon atom is denoted by a heavy continuous line, between an oxygen atom and a calcium atom by a dotted line, and between a boron atom and an oxygen atom by a light continuous line. The height of the atoms above the plane is given in terms of $c = 100$.

The method of formation of the B_2O_7 groups is best understood from this projection. Three Si_2O_7 groups each contribute two oxygen atoms (i. e., the corresponding base atoms across the reflexion plane) towards the construction of one B_2O_7 group. The group is completed by an O_5 oxygen lying on the reflexion plane. A continuous linkage between the Si_2O_7 groups is created in this way.

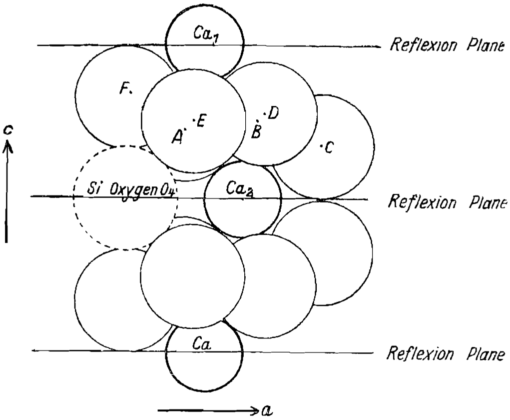

Fig. 6. Configuration of oxygen atoms surrounding a calcium atom.

Considering Fig. 4, the co-ordinates of the oxygen atoms O_1', O_2'', O_3, O_5' are $(-36^\circ, -72^\circ, 0^\circ)$, $(45^\circ, -130^\circ, -10^\circ)$, $(67\frac{1}{2}^\circ, -30^\circ, 30^\circ)$ and $(22\frac{1}{2}^\circ, -90^\circ, 90^\circ)$. The centres of gravity of the triangle O_1', O_3, O_5' and of the tetrahedron O_1', O_2'', O_3, O_5' are respectively the points $(18^\circ, -64^\circ, 40^\circ)$ and $(32^\circ, -80^\circ, 28^\circ)$. Since the co-ordinates assigned to the boron atom in this tetrahedron are $(22\frac{1}{2}^\circ, -67\frac{1}{2}^\circ, 45^\circ)$ it follows that the boron atom lies very nearly in one side of the tetrahedron rather than at its centre of gravity.

It will be seen that round alternate centres of symmetry in Fig. 5, six oxygen atoms are arranged in an elongated hexagonal formation. These atoms are very nearly in one plane, which is parallel to the reflexion planes. The way in which these atoms surround the calcium atoms is shown in Fig. 6, which is a projection of the arrangement on a plane perpendicular to the 'b' axis. The distances of the oxygen atoms A, B, C and D from the calcium atom Ca_2 are respectively 2.38 Å, 2.57 Å, 257 Å, 3.05 Å. Oxygen D has therefore a much stronger interest in Ca_1 than Ca_2. The number of oxygen atoms surrounding each calcium atom is eight.

The oxygen atom which is common to two BO_4 groups is only linked to the two boron atoms contained in these groups. The oxygen atoms forming the links between the Si_2O_7 groups and B_2O_7 groups are linked to one boron atom, one silicon atom and one calcium atom, except in the case of the O_3 atoms which are not very distant from another calcium atom. The silicon oxygen O_4, besides being linked to two silicon atoms, may possibly also be linked to two calcium atoms, although the distances O_4Ca_2 and O_4Ca_3 are a little large (3.46 Å and 3.73 Å respectively).

The ambiguity in sign of the 'c' parameter of the oxygen atom O_5 prohibits one from saying that the structure is unique, although in this paper we think we have presented the more likely alternative.

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Note added in proof:

Our best thanks are due to W. A. Wooster (Cambridge) who has since tested the Danburite crystal for piezoelectricity. The negative result of the test is in agreement with our choice of V_h^{16} as the true space group of the crystal.