THE CRYSTAL LATTICE OF ANHYDROUS SO-DIUM SULPHITE, Na₂SO₃

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Abstract

The crystal structure of Na_2SO_3 has been investigated by means of the Laue, the ionization, the rotation and the powder methods. The hexagonal unit cell containing two molecules was found to have dimensions: $a=5.441A$ $c=6.133A$. The observations seemed to be in conflict with all hexagonal and trigonal space groups. The difficulty was, however, overcome by assuming the crystals to be twins with the c-axis as twinning axis. The space group C_{3i}^1 was under this assumption found to be the only possible one. All parameters involved were determined from the observed intensities with the following result:

4 atoms Na in position $1a$ (000), $1b$ (00 $\frac{1}{2}$) and $2d$ ($\frac{1}{3}$ $\frac{2}{3}$ u_1), ($\frac{2}{3}$ $\frac{1}{3}$ $\bar{u}_1$) with $u_1=0.67$

2 atoms S in positions $2d$ ($\frac{1}{3}$ $\frac{2}{3}$ u_2), ($\frac{2}{3}$ $\frac{1}{3}$ $\bar{u}_2$) with $u_2=0.17$

6 atoms O in positions $6g(xyz)$, $(y-x,\bar{x},z)$, $(\bar{y},x-y,z)$, $(\bar{x}\bar{y}\bar{z})$, $(x-y,x,\bar{z})$, $(y,y-x,\bar{z})$ with $x=0.14$, $y=0.40$, $z=0.25$.

Two of the Na atoms are surrounded by 6 oxygens at a distance 2.469A; while the remaining two sodium atoms are surrounded by 3 oxygens at a distance 2.461A and by 3 at 2.870A. The structure shows the presence of groups SO_3. The distance from sulphur to the 3 surrounding oxygens is 1.39A, while the oxygens in the equilateral triangle have a distance of 2.24A. The sulphur atom has a displacement of 0.51A out of the plane of the oxygens. The form of the SO_3-group is thus like a low trigonal pyramid, being of the same type previously found for the groups $(ClO_3)^-$, $(BrO_3)^-$, $(AsO_3)^{-3}$ and $(SbO_3)^{-3}$.

1. Introduction

CRYSTALS of anhydrous sodium sulphite were first prepared and described by H. Hartley and W. H. Barrett.[1] The symmetry is reported as hexagonal, with an axial ratio $c/a=1.1246$. The crystals are short prisms with predominating forms (10.0) and (00.1) small faces (10.1), (10.2) and very small (11.1) faces. Further observations by Hartley and Barrett are: perfect cleavage parallel to (00.1); birefringence strong, negative; density at 15°C, 2.633.

2. Observations

Our chief interest in the x-ray analysis of the Na_2SO_3 was the determination of the shape and dimensions of the SO_3-group. In the following paragraphs we will describe the complete determination of the crystal structure. The investigation was started at the University of Manchester, where part of the observations were taken. Additional observations were collected in Ryerson Physical Laboratory, University of Chicago, where the investigation was completed.

[1] Hartley and Barrett, Trans. Chem. Soc. (London) 95, 1178 (1909).

Due to certain difficulties met during the investigation (see section 4), it became obvious that we must secure unusually reliable sets of observations, and apply as many different methods as possible. Our observations consist of the following.

(1) Complete rotation photographs and oscillation photographs around the hexagonal axis, and around the two different sets of horizontal axes. Oscillation angles of 5°, 15° and 30° were used. Crystal to plate distance was 5.0 cm. Radiation: $MoK\alpha$. Bernal's[2] graphical method of indexing the reflection spots was used throughout, thereby securing the most reliable indexing. In order to test the absence or presence of important reflexions many long exposures with an oscillation angle of 5° were taken.

(2) Laue photographs perpendicular to (00.1) and (10.0), and inclined a few degrees to the former directions. The photographs were indexed by converting the diagrams into gnomonic projection. The lower wave-length limit in the incident beam was tested on a number of known crystals.

(3) Intensity measurements on the ionization spectrometer of all reflections $hk.0$ up to 33.0 and of the reflexions 00.l. The series of intensities $hk.0$ was transformed into absolute measure by a method described in section 4, below. The crystal was completely bathed in the x-ray beam; the observed intensity was taken proportional to

$$|F|^2 \; 1+\cos^2 2\theta/\sin 2\theta,$$

where $|F|$ is the structure amplitude. $MoK\alpha$ radiation was used.

(4) Powder photographs with a high resolving camera, with sodium chloride as reference substance.[3] The unit cube of sodium chloride was assumed to have the edge $a = 5.628\text{A}$. The wave-length used was taken as $MoK\alpha_1 - \lambda = 0.70783\text{A}$.

3. The Unit Cell and Space Group Considerations

All observations agree with the following hexagonal cell:

$$a = 5.441 \pm 0.004\text{A} \quad c = 6.133 \pm 0.007\text{A} \quad c/a = 1.127$$

The correctness of the unit cell was carefully tested by means of long-exposure Laue photographs. No reflection spots could be found which indicated a larger unit cell than the one given above. By means of the directly determined density we find $1.98 \sim 2$ molecules of Na_2SO_3 connected with each unit cell. The calculated density for two molecules is 2.66.

The Laue photographs and the oscillation photographs possess the symmetry of the space groups $C_{3h}{}^n$, $C_6{}^n$ and $C_{6h}{}^n$. Vertical planes of symmetry are definitely not present.

A further limitation of the space groups was obtained through observations of the spectra 00.l. At ordinary exposures only the even order reflections from the base appear in the oscillation photographs. However, on several oscillation diagrams taken with 5° oscillation angle and long exposures the reflexion 00.3 was unmistakably present. These observations rule out all space groups save $C_{3h}{}^1$, $C_6{}^1$ and $C_{6h}{}^1$.

[2] Bernal, Proc. Roy. Soc. London A113, 117 (1926).
[3] We are indebted to Mr. F. Barta for taking the powder photographs.

4. THE DETERMINATION OF THE STRUCTURE

From an inspection of all our observations according to the four different methods certain regularities in the observed intensities at once become apparent, and will have to be accounted for by the atomic arrangement. We will consider only the intensities of reflections occurring at large values of $\sin\theta/\lambda$. These regularities we have collected in the following table:

I Reflexions $hk.0$

  (a) $2h+k=3n$ $(n=0, 1, 2, \cdots)$ Intensities are very strong

  (b) $2h+k\neq3n$ $(n=0, 1, 2, \cdots)$ Intensities are very weak or nil

II. Reflexions $hk.l$ with even l.

  (a) $2h+k=3n$ $(n=0, 1, 2, \cdots)$ Intensities are strong for $l=6$ and very weak or nil for $l=2, 4, 8$,

  (b) $2h+k\neq3n$ $(n=0, 1, 2, \cdots.)$ Intensities are very strong for $l=2, 4, 8,$; very weak or nil for $l=6$

III. Reflexions $hk.l$ with odd l.   Intensities are very weak or nil

These regularities are valid with no exceptions at large values of $\sin\theta/\lambda$, but do not fit the observations quite so well at small values of $\sin\theta/\lambda$ although giving a fairly good agreement. There is only one way of explaining this fact: the regularities given above must be characteristic of the cation lattice, but not for the oxygen lattice. Therefore the regularities will hold absolutely at large values of $\sin\theta/\lambda$, where the influence of the oxygen lattice with good approximation can be left out of consideration; but at small values of $\sin\theta/\lambda$ these regularities will be destroyed to some extent through the overlapping influence of the oxygen lattice.

In the unit cell we have 4 Na and 2 S atoms. As a first approximation we will consider the scattering power of sodium and sulphur to be the same. Our first problem will thus be to arrange 6 cations in the cell in such a way that the observed regularities in intensities of reflections are accounted for. (It has to be remembered that these 6 cations are of two kinds, so they cannot all be structurally equivalent.)

The regularity Ia and Ib tells us that the cations are evenly distributed on the 3 available threefold axes. As the c-axis has a length of only 6.13A, it is obvious that only 2 cations can lie on each axis, for otherwise cations would come closer than 2.04A, which is highly improbable. The positions of the cations are consequently according to regularity I: $00z_1$, $00z_2$, $\frac{1}{3}\frac{2}{3}z_3$, $\frac{1}{3}\frac{2}{3}z_4$, $\frac{2}{3}\frac{1}{3}z_5$, $\frac{2}{3}\frac{1}{3}z_6$.

The regularity III shows that the cations are situated along the threefold axes at intervals of $c/2$. Thus: $z_2=z_1+\frac{1}{2}$, $z_4=z_3+\frac{1}{2}$, $z_6=z_5+\frac{1}{2}$.

Finally the regularity given under II tells us that the cations are arranged in layers parallel to the c-face coming at intervals of $c/6$. We have thus: $z_3=z_1+\frac{2}{3}$, $z_5=z_1+\frac{1}{3}$ and the coordinates of the cations must be:

$$(00z)(00z+\tfrac{1}{2})(\tfrac{1}{3}\tfrac{2}{3}z+\tfrac{2}{3})(\tfrac{1}{3}\tfrac{2}{3}z+\tfrac{1}{6})(\tfrac{2}{3}\tfrac{1}{3}z+\tfrac{1}{3})(\tfrac{2}{3}\tfrac{1}{3}z+\tfrac{5}{6}).$$

This result is rather astonishing. The symmetry of the cation lattice is

that of D_{3d} only, while the observed symmetry is that of C_{6h}. We have as a matter of fact shown that no space group in the hexagonal and trigonal systems can account for the observations. The assumptions upon which we have based our deductions obviously cannot be correct. We have accordingly made a diligent search for a plausible explanation of the contradiction which exists between the observations.

An inspection of all our observations left no doubt as to the reported symmetry, neither could we find any other way of explaining the observed regularities than the one given above. The possibility of a bigger cell had also to be rejected from our observations. The assumption of another symmetry system likewise is highly improbable (it had to be either monoclinic or triclinic) with the nice development of the faces and the definitely uniaxial optical properties. Nor have we any justification for mistrusting the space group theory. We found rather that the only plausible explanation was to assume that all our observations were taken not on single crystals but on twins. We must emphasize, that we have not succeeded in finding direct evidence with which to back this assumption. Nevertheless the good agreement we have obtained between observed and calculated intensities assuming twinned crystals, as well as the plausibility of our final structure, must be taken as an indirect proof of the correctness of our assumption.

If the crystals are twins with the c-axis as twinning axis, the symmetry of our photographs would also be in agreement with that of the space groups $C_3{}^n$ and $C_{3i}{}^n$. Only $C_3{}^1$ and $C_{3i}{}^1$ can account for the observations in the 00.l spectra. *The distribution of the cations which we determined from the observed regularities also can be obtained from the special positions of these space groups.* The only difference between $C_3{}^1$ and $C_{3i}{}^1$ is the additional center of symmetry in the latter.

The oxygen atoms will have to lie in general positions (xyz) as no vertical planes of symmetry have been observed in the diagrams. The vertical distribution of the oxygen atoms with regard to the cation positions can easily be found from the spectra 00.l. The only odd order reflexion from the c-face which we observed is 00.3. This means that the oxygen atoms are lying in two layers parallel to the c-face at a distance of $c/2$. The fact that we have observed 00.3 with very small intensity cannot be interpreted as meaning that the oxygen layers have a distance slightly different from $c/2$, as we did not observe 00.5. But we must ascribe the presence of 00.3 to the difference in scattering power of Na and S, which means that the two sulphur atoms must lie on 2 different threefold axes. From the observed intensities of the even orders of 00.l and the known distribution of the cations along the c-axis we find that the oxygen layers parallel to the c-face must be displaced an amount $c/12$ against the cation layers. Summarizing our considerations so far we have found that the space group is $C_3{}^1$ or $C_{3i}{}^1$. We know the positions of the cations and the distribution in the c-direction of the oxygens referred to the cation lattice.

We have tried both space groups and finally selected $C_{3i}{}^1$ as the correct one. In fact a trial with $C_3{}^1$ showed that in order to get good agreement we had

to choose such values of the parameters as would give the symmetry of C_{3i}^1. The remaining unknown parameters in the structure were easily determined by means of the observed intensities.

As a final result we arrived at the following crystal structure which gave the best agreement with the observed intensities:

Space group C_{3i}^1.

Na in $1a: (000) + 1b\ (00\frac{1}{2}) + 2d\ (\frac{1}{3}\ \frac{2}{3}\ u_1)\ (\frac{2}{3}\ \frac{1}{3}\ \bar{u}_1)$ with $u_1 = 240°$

S in $2d: (\frac{1}{3}\ \frac{2}{3}\ u_2)\ (\frac{2}{3}\ \frac{1}{3}\ \bar{u}_2)$ with $u_2 = 60°$.

O in $6g \pm (xyz)\ (y-x, \bar{x}, z)\ (\bar{y}, x-y, z)$ with $x = 50°\ y = 145°$ and $z = 90°$

The very good agreement between observed and calculated intensities is seen from an inspection of the tables.

The F- curves used are given in Table VI. They are essentially the same as the Na, Cl and O F-curves used by one of us in the determination of structure of $NaClO_3$[4] and $NaClO_4$[5].

The relative intensities of the spectra $hk.0$ measured on the ionization spectrometer were transformed into absolute values by the following consideration; We assumed that the structure amplitude of the reflexion 33.0 was equal to 4 Na+2 S (chemical signs mean scattering power at the value of $\sin\theta/\lambda$ under consideration), as we with good approximation can leave the oxygen contribution out of consideration for such high values of $\sin\theta/\lambda$. All the observations were therefore reduced in such a way as to give an observed structure amplitude for 33.0 equalling the theoretical contribution of

TABLE I. *Ionization measurements in the prism zone.*

$hk.1$	Int.	$|F|$obs.	$|F|$calc.	$hk.0$	Int.	$|F|$obs.	$|F|$calc.
10.0	7.4	5	−6.7	31.0	5.4	8	−7.6
11.0	98.0	24	41.8	13.0	.5	2.5	.8
20.0	20.8	12	−11.6	40.0	3.1	7	−5.1
21.0	2.2	4.5	−4.7	32.0	1.3	4.5	−5.1
12.0	30.8	17	20.3	23.0	1.9	5.5	−5.5
30.0	76.0	28.5	33.7	41.0	42.8	27.5	28.4
22.0	70.4	29.5	33.0	14.0	21.6	19.5	18.6
				33.0	14.4	(17.5)	16.2

TABLE II. *Ionization measurements of spectra 00.l.*

$00.l$	Int.	$|F|$obs.	$|F|$calc.
00.1	nil	nil	2.1
00.2	81.6	20.8	−42.8
00.3	trace	trace	−5.2
00.4	12.0	11.9	16.8
00.5	nil	nil	2.3
00.6	9.6	(13.4)	13.4

[4] Zachariasen, Zeits. f. Krist. **71**, 517 (1929).

[5] Zachariasen, Zeits. f. Krist. **73**, 141 (1930).

TABLE III. *Results from powder photograph measurement.*

hk.l	$\sin^2\theta$	Int. obs.	$|F|^2 \cdot f$	hk.l	$\sin^2\theta$	Int. obs.	$|F|^2 \cdot f$
00.1	.00333	nil	1	22.1	.07107	nil	29
10.0	.00565	vw	45	31.0	.07340	vw	59
10.1	.00898	vs	919	20.4	.07590 }	m	{ 690
00.2	.01333	m	610	31.1	.07673 }		} 292
11.0	.01694	vs	1747	30.3	.08080 }	vvw	{ 107
10.2	.01898	vs	2852	22.2	.08107 }		{ 28
11.1	.02027	m	483	00.5	.08330	nil	2
20.0	.02259	w	135	31.2	.08673	ms	1599
20.1	.02592	m	387	10.5	.08895	nil	5
00.3	.02999 }	vw	{ 9	40.0	.09033	nil	26
11.2	.03027 }		{ 46	21.4	.09283 }	m	{ 2019
10.3	.03564 }	s-vs	{ 191	40.1	.09366 }		{ 70
20.2	.03592 }		{ 2322	22.3	.09773	nil	51
21.0	.03952	wm	434	11.5	.10024	nil	44
21.1	.04285	vvw	37	31.3	.10339 }		{ 102
11.3	.04693	w	215	40.2	.10366 }	m	{ 681
30.0	.05081	ms	1136	30.4	.10412 }		{ 22
20.3	.05258 }		{ 262	20.5	.10589	nil	150
21.2	.05285 }	s	{ 2104	32.0	.10726	nil	56
00.4	.05331 }		{ 94	32.1	.11059	vvw	102
30.1	.05414	nil	171	41.0	.11855 }		{ 1153
10.4	.05896	m	1035	00.6	.11995 }		{ 60
30.2	.06414	nil	1	40.3	.12032 }	ms	{ 16
22.0	.06774	ms	1089	32.2	.12059 }		{ 1128
21.3	.06951	nil	45	22.4	.12105 }		{ 4
11.4	.07025	vvw	76	41.1	.12188 }		{ 86

TABLE IV. *Results from Laue photographs.*

hk.l	Int. Obs.	$|F|$	hk.l	Int. Obs.	$|F|$
21.0	w	5	32.0	vvw	5
12.0	s	20	23.0	w	6
21.1	w	3	32.1	vw	14
12.1	m	7	23.1	nil	2
21.2	s	38	32.2	w	24
12.2	s	38	23.2	m	24
21.3	vw	7	41.0	vs	28
12.3	w	5	14.0	s	19
21.4	m	28	41.1	vvw	4
12.4	s	44	14.1	w	12
31.0	m	8	41.2	wm	17
13.0	w	1	14.2	vw	2
31.1	s	24	41.3	w	9
13.1	w	2	14.3	w	9
31.2	s	33	41.4	nil	5
13.2	s	29	14.4	w	9
31.3	wm	11			
13.3	w	6			
31.4	m	22			
13.4	s	23			

TABLE V. *Results of structure factor calculation.*

hk.l	$|F|$	$|F|^2$	$\Sigma|F|$	$\Sigma|F|^2$	Int. Obs. in osc. phot.
00.1	2.1	4	2	4	nil
00.2	−42.8	1832	43	1832	s
00.3	−5.2	27	5	27	vvw
00.4	16.8	282	17	282	m
00.5	2.3	5	2	5	nil
00.6	13.4	180	13	180	wm
10.0	−6.7	45	7	45	vw
10.1	−22.6	511⎫	43	919	ms
10.1̄	20.6	408⎭			
10.2	.6	—⎫	54	2852	vs
10.2̄	53.4	2852⎭			
10.3	12.7	161⎫	18	191	m
10.3̄	−5.5	30⎭			
10.4	31.9	1018⎫	36	1035	s
10.4̄	−4.1	17⎭			
10.5	−2.3	5⎫	2	5	nil
10.5̄	0	0⎭			
10.6	−1.4	2⎫	3	4	nil
10.6̄	−1.4	2⎭			
11.0	41.8	1747	42	1747	vs
11.1	−12.6	159⎫	31	483	m
11.1̄	18.0	324⎭			
11.2	−4.8	23⎫	10	46	w
11.2̄	−4.8	23⎭			
11.3	4.4	19⎫	18	215	wm
11.3̄	−14.0	196⎭			
11.4	−6.1	38⎫	12	76	w
11.4̄	−6.1	38⎭			
11.5	−2.1	4⎫	8	44	vw
11.5̄	6.3	40⎭			
11.6	20.5	420⎫	41	840	ms
11.6̄	20.5	420⎭			
20.0	−11.6	135	12	135	wm
20.1	−15.2	231⎫	28	387	m
20.1̄	12.5	156⎭			
20.2	48.0	2304⎫	52	2322	s
20.2̄	4.2	18⎭			
20.3	13.6	185⎫	22	262	w
20.3̄	−8.8	77⎭			
20.4	−5.9	35⎫	32	690	ms
20.4̄	25.6	655⎭			
20.5	−9.7	94⎫	17	150	w
20.5̄	7.5	56⎭			
21.0	−4.7	22	5	22	vw
21.1	.3	—⎫	3	7	o
21.1̄	−2.7	7⎭			
21.2	−.6	—⎫	38	1384	s
21.2̄	37.2	1384⎭			
21.3	−.9	1⎫	7	33	o
21.3̄	5.7	32⎭			
21.4	24.6	655⎫	28	666	m
21.4̄	−3.3	11⎭			
12.0	20.3	412	20	412	m
12.1	2.5	6⎫	7	30	vw
12.1̄	−4.9	24⎭			
12.2	17.2	296⎫	38	720	m
12.2̄	−20.6	424⎭			
12.3	2.4	6⎫	5	12	vw
12.3̄	2.4	6⎭			
12.4	8.0	64⎫	44	1353	m
12.4̄	35.9	1289⎭			

TABLE V. (*Continued*).

hk.l	$|F|$	$|F|^2$	$\Sigma|F|$	$\Sigma|F|^2$	Int. obs. in osc. phot.
30.0	33.7	1136	34	1136	vs
30.1	11.4	130 ⎫	18	171	w
30.1̄	−6.4	41 ⎭			
30.2	−.6	— ⎫	1	1	vvw
30.2̄	−.6	— ⎭			
30.3	−10.3	106 ⎫	11	107	w
30.3̄	1.1	1 ⎭			
30.4	−3.3	11 ⎫	7	22	nil
30.4̄	−3.3	11 ⎭			
22.0	33.0	1089	33	1089	vs
22.1	−.7	1 ⎫	6	29	vvw
22.1̄	5.3	28 ⎭			
22.2	−3.8	14 ⎫	8	28	vw
22.2̄	−3.8	14 ⎭			
22.3	−2.5	6 ⎫	9	51	vvw
22.3̄	−6.7	45 ⎭			
22.4	−1.5	2 ⎫	3	4	nil
22.4̄	−1.5	2 ⎭			
31.0	−7.6	58	8	58	w
31.1	10.7	115 ⎫	24	284	m
31.1̄	−13.0	169 ⎭			
31.2	30.6	936 ⎫	33	940	s
31.2̄	2.1	4 ⎭			
31.3	−3.4	12 ⎫	11	76	w
31.3̄	8.0	64 ⎭			
31.4	−4.8	23 ⎫	22	336	m
31.4̄	17.7	313 ⎭			
13.0	.8	1	1	1	vvvw
13.1	.2	— ⎫	2	4	vvw
13.1̄	−2.1	4 ⎭			
13.2	−3.0	9 ⎫	29	659	ms
13.2̄	25.5	650 ⎬			
13.3	−.5	⎭	6	26	vw
13.3̄	5.1	26 ⎫			
13.4	21.2	449 ⎫	23	451	m
13.4̄	−1.3	2 ⎭			
40.0	−5.1	26	5	26	vw
40.1	−6.9	48 ⎫	12	70	vw
40.1̄	4.7	22 ⎭			
40.2	0	0 ⎫	26	681	m
40.2̄	26.1	681 ⎭			
40.3	4.0	16 ⎫	5	16	vw
40.3̄	−.6	— ⎭			
40.4	16.7	279 ⎫	20	293	m
40.4̄	−3.7	14 ⎭			
32.0	−5.1	26	5	26	vw
32.1	−8.1	65 ⎫	14	99	w
32.1̄	5.8	34 ⎭			
32.2	.2	— ⎫	24	557	m
32.2̄	23.6	557 ⎭			
32.3	4.7	22 ⎫	5	22	vw
32.3̄	−.5	— ⎭			
32.4	14.8	219 ⎫	19	233	m
32.4̄	−3.8	14 ⎭			

TABLE V. (Continued).

hk.l	$|F|$	$|F|^2$	$\Sigma|F|$	$\Sigma|F|^2$	Int. obs. in osc. phot.
23.0	−5.5	30	6	30	vw
23.1	−1.6	3⎫	2	3	nil
23.$\bar{1}$	−.7	—⎭			
23.2	23.9	571⎫	24	571	m
23.$\bar{2}$	.5	—⎭			
23.3	5.0	25⎫	6	26	vw
23.$\bar{3}$	−.8	1⎭			
23.4	−4.1	17⎫	19	227	m
23.$\bar{4}$	14.5	210⎭			
41.0	28.4	807	28	807	s
41.1	2.3	5⎫	4	9	nil
41.$\bar{1}$	−2.0	4⎭			
41.2	−8.3	69⎫	17	138	wm
41.$\bar{2}$	−8.3	69⎭			
41.3	−4.5	20⎫	9	38	vw
41.$\bar{3}$	−4.3	18⎭			
41.4	2.5	6⎫	5	12	nil
41.$\bar{4}$	2.5	6⎭			
14.0	18.6	346	19	346	m
14.1	8.0	64⎫	12	77	vw
14.$\bar{1}$	−3.6	13⎭			
14.2	.8	1⎫	2	2	vw
14.$\bar{2}$	.8	1⎭			
14.3	−8.9	79⎫	9	79	w
14.$\bar{3}$	.1	—⎭			
14.4	−4.3	18⎫	9	36	vw
14.$\bar{4}$	−4.3	18⎭			

TABLE VI. F-curves.

$\sin\theta$	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
Na^+	9.6	8.5	7.1	5.8	4.6	3.6	2.8	2.0
S^{+4}	11.7	11.0	9.8	8.3	7.0	5.9	5.0	4.1
O^{-2}	9.0	7.1	5.4	3.9	2.6	1.8	1.2	.9

$4Na+2$ S, which we get from our F-curves. It will be seen from Tables I and II that extinction effects obviously have reduced the intensity of the stronger reflexions to a certain extent.

Due to the twinning with the c-axis as twinning axis, the reflections hk.l and hk.$\bar{l}$ having different intensities will fall on the same spot in all the photographs.

DISCUSSION OF THE STRUCTURE

In Fig. 1 is given a projection of the structure on the c-face. In the structure we can pick out groups SO_3. The structure of the SO_3-group is the one predicted by one of us.[6] The characteristic feature of the SO_3-group which distinguishes it from the CO_3 and NO_3 groups is the fact that the sulphur atom is displaced an amount $\Delta = 0.51$A out of the plane of the oxygen atoms. Analogous results have been found for other groups RO_3.[6] A more accurate

[6] W. H. Zachariasen, Vid. Akad. Skr. I Kl. No. 4 p. 142, 1928 Oslo; Zeits. f. Krist. 71, 527 (1929).

discussion of these results will be given in a following paper by one of us. The distance S–O is 1.39A.

There are two kinds of Na atoms in the structure, but both show the co-ordination number 6. The sodium atoms in positions (000) (00$\frac{1}{2}$) are sur-rounded by 6 oxygens forming the corners of a nearly regular octhahedron, the distance Na–O being 2.469A. The sodium atoms of the other kind have 3 oxygens at a distance 2.461A and 3 at a distance 2.870A. This oxygen octa-hedron is much distorted, and the sodium does not lie accurately in the center. The SO^3-groups share only corners with the Na$_I$-octahedra, while a face is shared with the Na$_{II}$-polyhedra. It is obvious that this sharing of a face in the
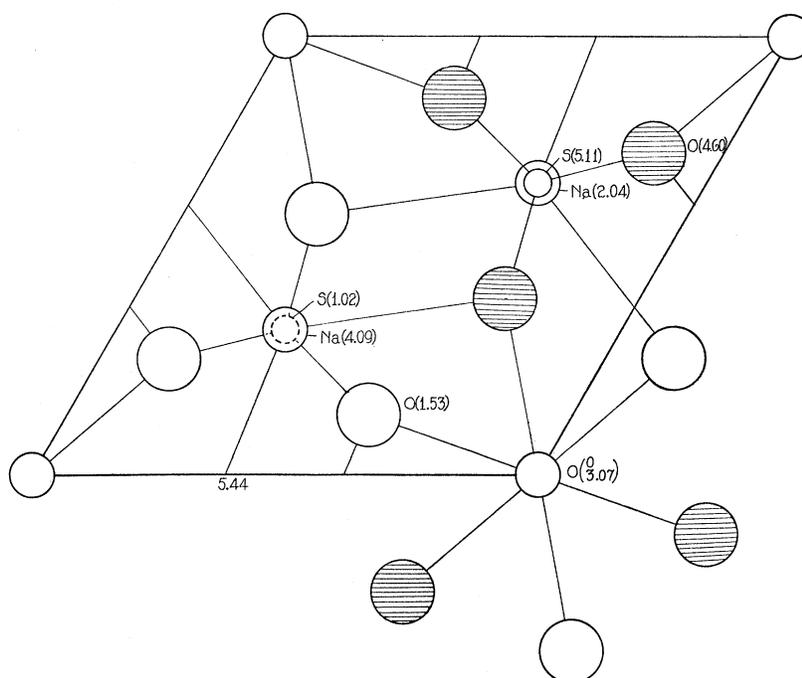
Fig. 1. Projection of the structure on (00.1). Numbers represent height of atoms above (00.1)-plane in A. Valency bonds are represented by connection lines.

latter case will cause some deformation.[7] In the first place we should expect a shortening of the edges bounding the shared face, that is the O–O distance in the SO^3-group will be shorter than normally. But we also should expect a dis-placement of the cations due to the one-sided configuration. This displacement we should expect to be greater for the cation with small valency; i.e., we should expect the sodium to be displaced in a direction away from the shared face. All these deformations are actually present: the displacement of the sodium atoms results in the two distances to oxygen. The shortening of the edges bounding the shared face will be noticed by a comparison of the SO$_3$-

[7] L. Pauling, Journ. Amer. Chem. Soc. 51, 1021 (1929).

group with the ClO₃-group. One finds namely that the O–O distance in the SO₃-group is smaller than in the ClO₃-group.

The reported strong negative birefringence of the crystals is a result of the fact that all the SO₃-groups are arranged with the plane of the oxygens parallel to the c-face. From a determination of the refractive indices one should be able to give an estimate of the O–O distance in the group. The cleavage parallel to the c-face is also in accordance with the structure.

Empirical observation shows the twinning probably is due to the existence of pseudo-elements of symmetry in the crystal structure. In the Na₂SO₃-structure the c-axis will be a pseudo twofold screw axis so the formation of twins with the c-axis as twinning axis can be explained. The fact that all the crystals we have examined according to our interpretation of the observations must be twins has worried us, and we must admit that we very strongly feel the lack of direct proof of the assumed twinning.

We tried to prepare etching figures on the crystals we had at our disposition. The result was not good but the figures we obtained did seem to indicate a polarity of the crystals. The symmetry of C_{3i}^1 does not give etching figures with the symmetry observed. It is a well-known fact however, that there are many examples where the etching figures indicate lower symmetry than that of the crystal. The results of etching experiments are thus not reliable.

The intensity calculations on the basis of our structure have, however, given so good agreement with all the observations we have collected that the principal correctness of our structure does not seem to be in doubt.

We are very much indebted to Dr. Hartley for providing us with crystals of Na₂SO₃.