The Crystal Lattice of Potassium Pyrosulphite, $K_2S_2O_5$, and the Structure of the Pyrosulphite Group[1]

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The crystal lattice of potassium pyrosulphite was examined in order to determine the structure of the pyrosulphite group. The Laue method and the oscillating crystal method were used. The dimensions of the monoclinic unit cell were found to be: $a = 6.95A$, $b = 6.19A$, $c = 7.55A$, $\beta = 102°41'$. The density determination gave 2.34 and corresponds to two molecules $K_2S_2O_5$ in the unit cell. The space group is $P2_1/m(C_{2h}^2)$. Two sets of four oxygen atoms are lying in general positions with coordinates $\pm(xyz)$ $\pm(x, \frac{1}{2}-y, z)$, while the remaining atoms are all lying in the reflection planes $\pm(u\frac{1}{4}v)$. The parameter values corresponding to the sixteen degrees of freedom were determined accurately and uniquely. No other assumptions than those underlying the theory for the diffraction of x-rays by crystals were made. The final parameters are:

	K I	K II	S I	S II	O I	O II	O III
x	0.22	0.65	0.70	0.01	0.07	0.63	0.67
y	0.25	0.25	0.25	0.25	0.06	0.06	0.25
z	0.95	0.67	0.22	0.32	0.24	0.31	0.03

In the lattice the potassium atoms are surrounded by nine or by seven oxygen atoms at average distances, respectively, of 3.01A and 2.78A. The pyrosulphite group can be described as a sulphite group and a sulphur dioxide molecule linked together by an electron pair bond between the two sulphur atoms. The sulphur to sulphur distance is 2.18A and the average sulphur to oxygen distance is 1.46A.* The atomic arrangement explains the observed cleavage and twinning.

1. INTRODUCTION

FOR several years the author has been interested in the determination of the shape and accurate dimensions of inorganic groups in crystals. The results of a large number of such investigations have been published in different journals during that time. However, there is yet a large field for studies along this line. Of the many different groups formed by sulphur and oxygen, for example, only the sulphate, the sulphite, and the dithionate groups have been examined.

It is a generally known fact that the determination of atomic arrangements involving 10 or more degrees of freedom is a problem of extreme difficulty. However, in many cases complicated crystal structures have been solved quite readily by utilizing empirical results deduced from already known atomic arrangements. To a large extent also chemical evidence has been used. However, when it is our object to get direct experimental data concerning the structure of unknown groups, it becomes clear that the purpose of the investigation fails, if the atomic arrangement is determined on the basis of assumptions of this kind.

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* The bonds formed by sulphur atoms, whether three or four in number, are directed towards the corners of a regular tetrahedron to a close degree of approximation.

[1] Some of the results of this paper were given in a Letter to the Editor, Phys. Rev. **40**, 113 (1932).

Some time ago I started upon an examination of the structure of potassium pyrosulphite with the chief object of finding the shape and dimensions of the pyrosulphite group. In agreement with the statements given above no assumptions other than those underlying the theory for the crystal diffraction effects have been used in determining the parameter values corresponding to the 16 degrees of freedom involved. The labor necessary to solve the problem accurately and uniquely on such a basis naturally has been extreme. Nevertheless I have tried as far as possible to prepare the following account of the investigation in such a manner that each successive step of the solution may be retraced.

Crystals of potassium pyrosulphite are described in Groth's Chemische Krystallographie.[2]

The symmetry is monoclinic prismatic with the following elements: $a:b:c = 1.4650:1:1.2222$, $\beta = 131°43'$. Twins on 001 are very common. The crystals show a perfect cleavage parallel to $10\bar{1}$. The birefringence is strong and negative. The plane of the optical axes is 010 and the acute bisectrix makes an angle of $1°10'$ with the c axis in the obtuse angle β. The angle between the optical axes is $2V = 76\frac{1}{2}°$ for Na light. The refractive indices are not given, nor is the density.

I prepared crystals of $K_2S_2O_5$ by evaporating a concentrated solution of potassium carbonate which had been oversaturated with sulphur dioxide. Care was taken in order to prevent oxidation during the evaporation. The crystals were thick prisms parallel to the b axis. Twins seemed to be more common than single individuals. The following faces were identified: 102, $10\bar{1}$, $20\bar{1}$, 001, 110 and 210. An excellent crystal of approximate dimensions $0.7 \times 1.5 \times 0.7$ mm was selected, and all the observations were taken on this crystal. The density was determined by the suspension method and gave the value 2.34.

2. Experimental Methods

The Laue method and the oscillating crystal method were used. The photographs were indexed by means of the ordinary graphical methods,

Laue photographs were taken with the incident beam parallel to the three crystallographic axes and with the beam perpendicular to the a and c face. The lower wave-length limit in the incident beam was 0.27A and had been checked on a number of known crystals.

For the oscillation method Mo $K\alpha$ radiation was employed. The distance from crystal to photographic plate was 5.00 cm and was calibrated by means of calcite photographs. With the photographic plate at right angles to the incident beam reflections with glancing angles up to about 20° could be recorded. However, in several instances it was found desirable to measure reflections with greater glancing angles; the photographic plate was then set so as to make an angle of 30° with the direct beam. During each exposure the crystal was oscillated through 15°.

Thirty-five different photographs were taken and completely indexed,

² P. Groth, Chemische Krystallographie 2, 305, Leipzig, 1908.

and the intensity of some 700 reflections from different atomic planes was recorded. In this manner all possible reflections with $\sin\theta/\lambda$ less than 0.5 were measured and in addition a large number of reflections with $\sin\theta/\lambda$ between 0.5 and 0.86. A suitable selection of about half of the observations are compiled in Tables IV, V, VI and VIII.

The F curve values used in the investigation were taken from James and Brindley's recent paper[3] and are given in Table I. In accordance with modern

TABLE I. *F curve values.*

$\sin\theta/\lambda$	0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
K^{+1}	18	16.5	13.3	10.8	8.9	7.8	7.0	6.4	5.9	5.3
S^{+1}	14	12.1	10.1	8.8	7.8	6.9	6.0	5.2	4.5	3.9
O^{-1}	9	7.5	5.4	3.8	2.8	2.1	1.8	1.55	1.50	1.4

views the state of ionization was taken as K^{+1}, S^{+2}, O^{-1}. This assumption has no real physical meaning and is also of little consequence as far as the numerical values of the scattering powers are concerned, because of the small contribution from the valence electrons in the regions of $\sin\theta/\lambda$ where we have observations. The F curve values in Table I are not corrected for thermal motion; as we have only relative intensity measurements this correction is of little importance.

3. UNIT CELL AND SPACE GROUP

The choice of axes given by Groth is not very satisfactory. I have found it desirable to change the direction of the crystallographic a-axis so as to correspond to an angle β which is closer to 90°. This is accomplished by taking the a-axis in the direction with zone indices $[10\bar{1}]$. The new crystallographic elements then become: $a:b:c = 1.1212:1:1.2222$, $\beta = 102°\ 41'$. If $h'k'l'$ are the Miller indices referred to Groth's axes, hkl the Miller indices in the new set of axes, the transformation formulae will be: $h = -h' - l'$ $k = k'\ l = l'$. In the following all indices are referred to the new axes.

All the observations agree with the following unit cell: $a = 6.95$A $b = 6.19$A $c = 7.55$A $\beta = 102°\ 41'$. The axial lengths are accurate to 0.02A. The axial ratios are: 1.123:1:1.220.

The observed density of 2.34 gives two (2.02) molecules in the unit cell. The calculated density is, conversely, 2.31.

The only class of absent reflections are the odd orders from 010. As the symmetry is monoclinic prismatic all space groups except the holohedral ones must be rejected. All the space groups except $P2/m(C_{2h}^1)$ and $P2_1/m$ (C_{2h}^2) are ruled out through observed reflections. The absence of odd orders from 010 shows that the b axis is a screw axis rather than a rotation axis. We conclude therefore that $P2_1/m$ is the correct space group.

4. DISTRIBUTION OF THE ATOMS AMONG THE AVAILABLE POSITIONS OF THE SPACE GROUP

In the space group $P2_1/m$ we may have twofold or fourfold positions. We get twofold positions by placing the atoms in centers of symmetry or in

[3] James and Brindley, Zeitschr. f. Krist. **78,** 470 (1931).

the reflection planes. The coordinates of the atoms are: centers of symmetry: $(000)(0\frac{1}{2}0)$, $(\frac{1}{2}00)(\frac{1}{2}\frac{1}{2}0)$, $(00\frac{1}{2})(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; Reflection planes: $\pm(u\frac{1}{4}v)$. The fourfold positions correspond to coordinates: $\pm(xyz)\pm(x, \frac{1}{2}-y, z)$.

Since there are ten oxygen atoms in the unit cell, it follows that at least two of them must lie in centers of symmetry or in reflection planes.

For reflections with $\sin\theta/\lambda$ greater than 0.4 we may with good approximation leave the oxygen contribution out of consideration because of the small scattering power. As the reflections 060,080 and 0.10.0 all are exceptionally strong, it follows that the contributions from potassium and sulphur atoms must be in phase. The potassium and sulphur atoms therefore must all have coordinates zero in direction of the b-axis, or they must all have coordinates $\frac{1}{4}$. The former possibility must be rejected as it cannot account for the great intensity of reflections from planes with odd index k (e.g., 510 and 470). Consequently the potassium and sulphur atoms all lie in the reflection planes; i.e. 2K I in $\pm(u_1\frac{1}{4}v_1)$, 2K II in $\pm(u_2\frac{1}{4}v_2)$, 2S I in $\pm(u_3\frac{1}{4}v_3)$ and 2S II in $\pm(u_4\frac{1}{4}v_4)$.

The contribution from potassium and sulphur to the structure amplitude of a reflection hkl is: a. k even,

$$(-1)^{k/2}2\left[K\left[\cos 2\pi(hu_1+lv_1)+\cos 2\pi(hu_2+lv_2)\right]\right.$$
$$\left.+S\left[\cos 2\pi(hu_3+lv_3)+\cos 2\pi(hu_4+lv_4)\right]\right]$$

b. k odd,

$$(-1)^{(k+1)/2}2\left[K\left[\sin 2\pi(hu_1+lv_1)+\sin 2\pi(hu_2+lv_2)\right]\right.$$
$$\left.+S\left[\sin 2\pi(hu_3+lv_3)+\sin 2\pi(hu_4+lv_4)\right]\right]$$

It is seen from these expressions that, except for the decrease in scattering power with increasing k, the contribution from potassium and sulphur is the same for reflections $h0l$, $h2l$, $h4l$ . . . with constant h and l, and also for reflections $h1l$, $h3l$, $h5l$ . . . If the oxygen atoms have no effect, or if they are lying all in the reflection planes, the intensities of reflection in the series $h0l$, $h2l$, $h4l$ . . . and $h1l$, $h3l$, $h5l$ . . . will decrease regularly with increasing k. This is not the case as the observations of Table III definitely show. In order to account for the great deviations from such a regular decrease it becomes necessary to put two sets of four oxygen atoms in general positions; i.e.,

$$4 \text{ O I in} \pm (x_1y_1z_1) \pm (x_1\tfrac{1}{2}-y_1z_1)$$
$$4 \text{ O II in} \pm (x_2y_2z_2) \pm (x_2\tfrac{1}{2}-y_2z_2).$$

At this stage of the investigation it is hardly possible to decide with any degree of certainty whether the two remaining oxygen atoms are situated in centers of symmetry or in reflection planes. This question we will therefore try to settle later (see page 929).

5. DETERMINATION OF PARAMETERS FOR OXYGEN ATOMS IN GENERAL POSITIONS

The observed intensities for the different $0k0$ reflections are given in Table II. The structure amplitudes are as follows (neglecting the contribution from the oxygen atoms in twofold positions).

TABLE II. *Reflections* 0k0.*

0k0:	020	040	060	080	0.10.0
sin θ/λ:	0.1616	0.3231	0.4847	0.6462	0.8078
Int. obs.:	vs	vs	ms	w	w—

TABLE III. *Prominent differences in intensity due to oxygen contribution.*

h0l	001 vw	002 vs	20$\bar{1}$ nil	201 vs	300 vs	103 nil	40$\bar{3}$ nil	10$\bar{5}$ w
h2l	021 wm	022 vw	22$\bar{1}$ vs	221 nil	320 w	123 w	42$\bar{3}$ m	12$\bar{5}$ s
h4l	041 vvw	042 w	24$\bar{1}$ w	241 w	340 m	143 vvw	44$\bar{3}$ vw	14$\bar{5}$ m
h1l	210 vs	013 ms	212 m—	11$\bar{4}$ w	410 w			
h3l	230 w	033 w—	232 nil	13$\bar{4}$ s	430 m			
h5l	250 m	053 w			450 vw			

* In this table and in subsequent tables the intensities are indicated in the order vvs, vs, s, ms, mw, w, vw, vvw, and nil. (v = very, s = strong, m = medium, w = weak).

$$(-1)^{k/2}(4K + 4S) + 4O(\cos 2\pi k y_1 + \cos 2\pi k y_2).$$

If the general decrease of intensity with increasing glancing angle is taken into consideration it becomes apparent that the fourth, sixth and tenth order are exceptionally strong reflections, whereas the second and eighth are relatively weak. These observations are explained if we choose:

$$2\pi y_1 = 20° \qquad 2\pi y_2 = 20°.$$

We will next try to fix the parameters x_1 and x_2 by making use of the observed intensities for reflections $hk0$ complied in Table IV. The structure amplitude for these reflections takes the form:
a. k even,

$$(-1)^{k/2}2[K[\cos 2\pi h u_1 + \cos 2\pi h u_2] + S(\cos 2\pi h u_3 + \cos 2\pi h u_4)]$$
$$+ 4\,O\cos k20°[\cos 2\pi h x_1 + \cos 2\pi h x_2]$$

b. k odd,

$$(-1)^{(k+1)/2}2[K(\sin 2\pi h u_1 + \sin 2\pi h u_2) + S(\sin 2\pi h u_3 + \sin 2\pi h u_4)]$$
$$- 4\,O\sin k20°[\sin 2\pi h x_1 + \sin 2\pi h x_2].$$

From considerations of the relative intensities of reflections $h00$, $h20$, $h40$ ... and of reflections $h10$, $h30$, $h50$ ... the following conclusions as to the magnitude of $\cos 2\pi h x_1 + \cos 2\pi h x_2$ and of $\sin 2\pi h x_1 + \sin 2\pi h x_2$ can be drawn:

$h=$	$\cos 2\pi h x_1 + \cos 2\pi h x_2$	$\sin 2\pi h x_1 + \sin 2\pi h x_2$
1	very small	small
2	medium small	very large
3	large	very small
4	large	medium large
5	small	large
6	medium small	small
7	large	small

Because of the space group symmetry, we may arbitrarily choose the parameter x_1 such that $0° < 2\pi x_1 < 90°$. The large value of $\sin 2\pi 2x_1 + \sin 2\pi 2x_2$ indicates parameters close to $45°$ and $225°$. It is easily deduced from the above list that only the following two sets of parameter values are possible:

$$2\pi x_1 = 25°, \quad 2\pi x_2 = 225°; \quad \text{or} \quad 2\pi x_1 = 45°, \quad 2\pi x_2 = 205°,$$

TABLE IV. *Reflections hk0.*

sin θ/λ→	index	0.0737	0.1474	0.2211	0.2948	0.3685	0.4422	0.5159
0.0808	010 nil 0	100 vvw 6	200 w −23	300 vs 77	400 vw −2	500 vvw 10	600 vw− 22	700 w− −25
0.1616	020 vs −75	110 m 32	210 vs −80	310 vvw 12	410 w 40	510 m −50	610 w− −24	710 nil 15
0.2423	030 nil 0	120 vw 3	220 m 44	320 w −39	420 w− −28	520 vw −7	620 w− −36	720 nil 0
0.3231	040 vs 86	130 vw −16	230 w 26	330 vw −13	430 m −49	530 w− 29	630 w− 30	
0.4039	050 nil 0	140 nil 3	240 w− −24	340 m− 45	440 nil 15	540 vvw 8	640 vw− 27	
0.4847	060 ms −73	150 vw 19	250 m −56	350 nil 6	450 vw 25	550 w −48		
0.5655	070 nil 0	160 nil −4	260 vw 15	360 w− −39	460 nil −7	560 nil −8		
0.6462	080 w 40	170 vw −11	270 w− 23	370 nil −8	470 w −31	570 vw 25		
0.7270	090 nil 0	180 nil 2	280 w− −20	380 w− 23	480 vvw 17	580 nil 5		
0.8078	0.10.0 w− −45	190 nil 10	290 vw −27	390 vvw 8	490 vw 24	590 vw −26		
		1.10.0 nil −2	2.10.0 vvw 11	3.10.0 w− −29	4.10.0 nil −2			

TABLE V. *Reflections 0kl.*

sin θ/λ→	index	0.0679	0.1357	0.2036	0.2714	0.3393	0.4072	0.4750
0.0808	010 nil 0	001 vw 16	002 vs −61	003 vs −71	004 w 29	005 w −17	006 nil 14	007 w −37
0.1616	020 vs −75	011 m −28	012 vw −2	013 m 49	014 w 26	015 w −7	016 nil 5	017 vw− 11
0.2423	030 nil 0	021 w −23	022 vw −12	023 s −43	024 vvw 4	025 w− 3	026 nil −19	027 w− 32
0.3231	040 vs 86	031 w −23	032 nil 5	033 w− −15	034 w −32	035 nil −3		
0.4039	050 nil 0	041 vvw 11	042 w −19	043 w 41	044 nil 9	045 vw −9		
0.4847	060 ms −73	051 w −30	052 nil −3	053 w 41	054 vw− 16	055 nil −8		
0.5655	070 nil 0	061 nil −7	062 w− 20	063 w −35	064 nil −10	065 vvw 10		
0.6462	080 w 40	071 nil −3	072 nil −3	073 vvw −16	074 vw −22	075 nil 0		
0.7270	090 nil 0	081 nil 8	082 vw 1	083 vw 24	084 nil −1			
0.8078	0.10.0 w− −45	091 nil −5	092 nil 0	093 vvw 20	094 nil 17			
		0.10.1 nil −5	0.10.2 vvw 18	0.10.3 vvw −27				

These two sets are, however, equally justified as we can derive one from the other; it is therefore immaterial which of the two sets we choose. We therefore take:

$$2\pi x_1 = 25°, \quad 2\pi x_2 = 225°.$$

In order to determine the parameters z_1 and z_2 we proceed in a similar manner. From the observations compiled in Table V for reflections $0kl$ the following results are obtained

$l=$	$\cos 2\pi l z_1 + \cos 2\pi l z_2$	$\sin 2\pi l z_1 + \sin 2\pi l z_2$
1	small	very large
2	very large	very small
3	small	large
4	medium small	medium small
5	small	small
6	very small	very small
7	very small	

It is at once apparent from these conclusions that $2\pi z_1$ and $2\pi z_2$ both must be close to 90°. The most accurate parameter values were found on the basis of our observations for reflections $h0l$, $h2l$, $h4l$ . . . and $h1l$, $h3l$, $h5l$ . . . using the values for x_1 and x_2 which we determined previously. The final results of these calculations are:

$$2\pi z_1 = 85°, \quad 2\pi z_2 = 110°.$$

We are thus in the interesting situation that we have been able to fix the positions of some of the atoms without knowing anything about the arrangement of the rest of the atoms.

6. Determination of Parameter Values for Potassium and Sulphur Atoms

Knowing the oxygen lattice we can from an inspection of the observations on the basis of the expression for the structure amplitude, get definite information about the potassium plus sulphur contribution for each individual reflection.

The difference in scattering power between potassium and sulphur is small, in fact so small that it seems impossible to distinguish a potassium atom from a sulphur atom by means of intensity considerations alone. For a time we will therefore treat the potassium and sulphur atoms as if they were alike and give them a scattering power of $\frac{1}{2}(K+S)$. When we have fixed the positions of all the atoms in the unit cell, we will try to find a method by means of which a distinction can be made.

Let us at first determine the 4 parameters in the direction of the a axis, namely u_1 u_2 u_3 and u_4. For that purpose the observed intensities of reflections $hk0$ have to be used. Having determined the oxygen positions we are able to calculate the contribution of the oxygen atoms to the structure amplitude. We have, for example:

300 $\quad 2K(S)\left[\cos 2\pi 3u_1 + \cos 2\pi 3u_2 + \cos 2\pi 3u_3 + \cos 2\pi 3u_4\right] + 3.88O \quad vs$

320 $\quad - 2K(S)\left[\cos 2\pi 3u_1 + \cos 2\pi 3u_2 + \cos 2\pi 3u_3 + \cos 2\pi 3u_4\right] + 2.99O \quad w$

340 $\quad 2K(S)\left[\cos 2\pi 3u_1 + \cos 2\pi 3u_2 + \cos 2\pi 3u_3 + \cos 2\pi 3u_4\right] + 0.66O \quad m$

In order to account for these observations we must have $\cos 2\pi 3u_1 +$ $\cos 2\pi 3u_2 + \cos 2\pi 3u_3 + \cos 2\pi 3u_4$ very large and positive. Proceeding in this manner for all observations in Table IV we get the following conclusions:

$$\cos 2\pi hu_1 + \cos 2\pi hu_2 + \cos 2\pi hu_3 + \cos 2\pi hu_4 \qquad \sin 2\pi hu_1 + \sin 2\pi hu_2 + \sin 2\pi hu_3 + \sin 2\pi hu_4$$

$h=1$	very small	small negative
2	medium large negative	very large positive
3	very large positive	very small
4	medium large positive	large negative
5	very small	large positive
6	medium small positive	medium large
7	medium large	very small

It is our task then to find values of the four parameters which satisfy the above results. This necessarily requires lengthy calculations, but can nevertheless be carried out uniquely. Definite starting points for the calculations are readily found. The very large contribution to the 210 reflection shows definitely that all the parameters lie within the ranges $0-0.25$ $0.50-0.75$. Since the contribution to the reflection 510 also is very large we must look for values in the ranges $0-0.10$ $0.20-0.25$ $0.60-0.70$. By continued calculations of this kind we can eventually find the accurate values. The best agreement was obtained with the following set: $2\pi u_1 = 80°$, $2\pi u_2 = 235°$, $2\pi u_3 = 250°$, $2\pi u_4 = 5°$. No other essentially different set can account for the observations.

The determination of the parameters v_1 v_2 v_3 and v_4 is carried out in the same manner. Besides the observations collected in Table V we are, however,

TABLE VI. *Reflections h0l.*

h00	I	F	h01	I	F	h02	I	F	h03	I	F	h04	I	F	h05	I	F	h06	I	F
600	vw −	22																		
500	vvw	10	501	vvw	−9	502	w	12												
400	vw	−2	401	nil	0	402	w	30	403	w	−14	404	w	−25						
300	vs	77	301	s	−55	302	ms	−66	303	m	38	304	vvw	0	305	w	−34			
200	w	−23	201	vs	−68	202	wm	−39	203	m −	35	204	nil	6	205	w	−37			
100	vvw	6	101	m	30	102	m	−28	103	nil	1	104	w	18	105	m	39	106	vw −	14
001	vw	16	002	vs	−61	003	vs	−71	004	w	29	005	тw	−17	006	ni	14			
$\bar{1}$00	vvw	6	$\bar{1}$01	w	−13	$\bar{1}$02	s	−49	$\bar{1}$03	wm	−27	$\bar{1}$04	w −	−4	$\bar{1}$05	wm	−43	$\bar{1}$06	vw −	−33
$\bar{2}$00	w	−23	$\bar{2}$01	nil	−4	$\bar{2}$02	w	−24	$\bar{2}$03	m	−42	$\bar{2}$04	w	−21	$\bar{2}$05	vw	11	$\bar{2}$06	w	14
$\bar{3}$00	vs	77	$\bar{3}$01	w	10	$\bar{3}$02	ms	−36	$\bar{3}$03	wm	41	$\bar{3}$04	w −	14	$\bar{3}$05	nil	14	$\bar{3}$06	m	60
$\bar{4}$00	vw	−2	$\bar{4}$01	wm	37	$\bar{4}$02	vw	5	$\bar{4}$03	nil	−1	$\bar{4}$04	w	33	$\bar{4}$05	vvw	−3	$\bar{4}$06	vw	−18
$\bar{5}$00	vvw	10	$\bar{5}$01	vw	7	$\bar{5}$02	vw	16	$\bar{5}$03	w	8	$\bar{5}$04	w	−31	$\bar{5}$05	vw	−23			
$\bar{6}$00	vw −	22	$\bar{6}$01	vvw	2	$\bar{6}$02	w	−26	$\bar{6}$03	vvw	1									

now also able to utilize the observed intensities of reflections hkl. From detailed calculations it can be shown that there is only one set of values which can satisfactorily account for the observations, namely the following:

$$2\pi v_1 = 340°, \quad 2\pi v_2 = 240°, \quad 2\pi v_3 = 80°, \quad 2\pi v_4 = 115°.$$

7. DETERMINATION OF PARAMETERS FOR OXYGEN ATOMS IN TWOFOLD POSITIONS

The effect on the intensity of the oxygen atoms in twofold positions we have so far left out of consideration. This effect is small because there are only two of these atoms and because their scattering power is small. However it is certainly large enough to be detected at small values of $\sin\theta/\lambda$. The parameters which we already have determined must be very accurate as there is a satisfactory agreement between observed and calculated intensities even for reflections corresponding to very large $\sin\theta/\lambda$.

If therefore discrepancies exist at small values of $\sin\theta/\lambda$, they cannot be accounted for by changes in the parameter values, and must consequently be attributed to the effect of the two oxygen atoms. In Table VII are seen a number of such discrepancies.

TABLE VII. *Calculated amplitudes without contributions from oxygen atoms in twofold positions.*

$h0l$	I	F	$h1l$	I	F	$h2l$	I	F	$h3l$	I	F
001	vw	0	011	m	−26	021	m	−13	031	wm	−24
100	vvw	14	110	m	19	120	vw	−4	130	w	−8
10$\bar{1}$	w	−3	11$\bar{1}$	nil	−10	12$\bar{1}$	w−	9	13$\bar{1}$	nil	7
101	m	27	111	vs	−67	121	nil	0	131	s	40
002	vs	−74	012	vw	6	022	vw	−3	032	nil	−8
10$\bar{2}$	s	−39	11$\bar{2}$	vs	−84	12$\bar{2}$	s	41	13$\bar{2}$	vs	78
200	w	−17	210	vs	−68	220	m	39	230	wm	19
20$\bar{1}$	nil	1	21$\bar{1}$	w	32	21$\bar{1}$	vs	64	23$\bar{1}$	nil	−6
102	m	30	112	vvw	−20	122	s	−58	132	vvw	1
201	vs	−61	211	w	−19	221	nil	−3	231	vw	8
20$\bar{2}$	w	−22	21$\bar{2}$	w−	20	22$\bar{2}$	w	−20	23$\bar{2}$	w	16
10$\bar{3}$	wm	−17	11$\bar{3}$	nil	−5	12$\bar{3}$	nil	−15	13$\bar{3}$	nil	8

For example, the calculated structure amplitude for the 100 reflection is too large, while it is too low for 110 and 120. The fact that discrepancies occur for reflections with odd k shows that the two oxygen atoms must lie in the reflection planes, i.e., $\pm(u_5\frac{1}{4}v_5)\cdot\cos 2\pi u_5$ and $\sin 2\pi u_5$ must be negative in order to explain the discrepancies mentioned; consequently $2\pi u_5$ must lie between 180° and 270°. The calculated structure amplitudes for the reflections 001, 011, 021 are all too low; $2\pi v_5$ must therefore lie between 0° and 90°. Detailed calculations of this kind give as result the accurate values:

$$2\pi u_5 = 240°, \quad 2\pi v_5 = 10°.$$

8. THE FINAL PARAMETER VALUES

We have thus been able to determine all the 16 parameters in the structure on the basis of observed intensities alone. From careful considerations an accuracy of ± 0.01 can be claimed for all values except u_5 and v_5. For the latter parameters the accuracy is of the order ± 0.03. I wish to emphasize that the determination is unique; no other set of parameter values essentially different from the one given can account for the observed intensities. The agreement between observation and calculation no doubt can be slightly improved at large values of $\sin\theta/\lambda$ by minute changes in the parameter values within the limits given. No weight can be given to minor discrepanices due to the fact that the scattering power may be different in different directions from lack of spherical symmetry.

As previously stated we cannot distinguish between a potassium and a sulphur atom by means of intensity considerations alone. A large number of atomic arrangements containing potassium and oxygen atoms are known with great accuracy. The closest distance ever observed between potassium and oxygen atoms is of the order 2.7A. In the potassium pyrosulphite structure the atoms with coordinates u_1v_1 and u_2v_2 all have distances from adjacent oxygen atoms greater than 2.69A, whereas the atoms with coordinates u_3v_3

and u_4v_4 have distances from oxygen atoms as low as 1.45 and 1.44A. It is therefore reasonable to conclude that the former atoms are potassium, the latter sulphur.

The structure amplitudes calculated on the basis of the determined parameter values and with the proper F curve values are given in the Table IV, V, VI and VIII.

TABLE VIII. *Reflections hkl. I* is observed intensity; F is the calculated structure amplitude.

$\sin\theta/\lambda$	h0l	I	F	h1l	I	F	h2l	I	F	h3l	I	F	h4l	I	F
0.0679	001	vw	16	011	m	−28	021	m	−23	031	wm	−23	041	vvw	11
0.0737	100	vvw	6	110	m	32	120	vw	3	130	w	−16	140	vvw	3
0.0885	10$\bar1$	w	−13	11$\bar1$	nil	−1	12$\bar1$	w−	17	13$\bar1$	nil	0	14$\bar1$	w	−9
0.1106	101	m	30	111	vs	−55	121	nil	4	131	s	32	141	vw	7
0.1357	002	vs	−61	012	vw	2	022	vw	−12	032	nil	5	042	w	−19
0.1395	10$\bar2$	s	−49	11$\bar2$	vs	−76	12$\bar2$	s	49	13$\bar2$	vs	73	14$\bar2$	ms	−35
0.1474	200	w	−23	210	vs	−80	220	m	44	230	wm	26	240	w	−24
0.1481	20$\bar1$	nil	−4	21$\bar1$	w	20	22$\bar1$	vs	67	23$\bar1$	nil	1	24$\bar1$	w	−25
0.1680	102	m	28	112	vvw	−9	12$\bar2$	s	−56	13$\bar2$	vvw	−7	14$\bar2$	m−	31
0.1752	201	vs	−68	211	w	−27	221	nil	3	231	vw	14	241	w	−25
0.1770	20$\bar2$	w	−24	21$\bar2$	w−	9	22$\bar2$	w	−19	23$\bar2$	w	23	24$\bar2$	nil	1
0.2007	10$\bar3$	wm	−27	11$\bar3$	nil	0	12$\bar3$	nil	−7	13$\bar3$	nil	5	14$\bar3$	nil	−1
0.2036	003	vs	−71	013	ms	49	023	s−	−43	033	w−	−15	043	m	41
0.2165	30$\bar1$	w	10	31$\bar1$	m−	40	32$\bar1$	vw−	−6	33$\bar1$	w	−24	34$\bar1$	vw−	5
0.2211	300	vs	77	310	vvw	12	320	wm	−39	330	vw	−13	340	m	45
0.2212	202	wm	−39	212	m−	35	222	w	31	232	nil	−5	242	vw	−25
0.2235	20$\bar3$	m	−42	21$\bar3$	w−	−15	22$\bar3$	vw	−5	23$\bar3$	vw−	−12	24$\bar3$	vvw	−11
0.2312	103	nil	1	113	w	16	123	w	−24	133	vvw	7	143	vvw	10
0.2326	30$\bar2$	ms	−36	31$\bar2$	s	47	32$\bar2$	m	28	33$\bar2$	m	−38	34$\bar2$	w	−28
0.2451	301	s	−55	311	vw	−9	321	m	35	331	vw−	−11	341	m	−37
0.2651	10$\bar4$	w−	−4	11$\bar4$	w	25	12$\bar4$	vvw	0	13$\bar4$	s	−44	14$\bar4$	vvw	0
0.2655	30$\bar3$	wm	41	31$\bar3$	w−	13	32$\bar3$	wm	−38	33$\bar3$	vw−	−5	34$\bar3$	w	29
0.2714	004	w	29	014	w	26	024	nil	4	034	w	−32	044	nil	9
0.2763	203	m−	35	213	s	−51	223	vw	−4	233	m	42	243	w	17
0.2790	20$\bar4$	vw	−21	21$\bar4$	wm	40	22$\bar4$	m	58	23$\bar4$	wm	−52	24$\bar4$	w	−31
0.2837	302	ms	−66	312	vw−	7	322	w−	26	332	nil	6	342	wm	−39
0.2876	40$\bar1$	wm	37	41$\bar1$	m	37	42$\bar1$	nil	−4	43$\bar1$	m	−49	44$\bar1$	vw	15
0.2948	400	vw	−2	410	wm	40	420	w−	−28	430	m	−49	440	nil	15
0.2962	40$\bar2$	vw	5	41$\bar2$	m−	−32	42$\bar2$	w−	23	43$\bar2$	m	53	44$\bar2$	nil	−8
0.2964	104	w	18	114	nil	−16	124	w	22	134	w−	26	144	nil	−4
0.3101	30$\bar4$	w−	14	31$\bar4$	nil	−2	32$\bar4$	w	−29	33$\bar4$	nil	−1	3$\overline{44}$	w−	17
0.3167	401	nil	0	411	nil	−3	421	vvw	−15	431	w−	18	441	nil	6
0.3193	40$\bar3$	nil	−1	41$\bar3$	vw	−7	42$\bar3$	m	−41	43$\bar3$	w	20	44$\bar3$	vw	19
0.3310	105	wm	−43	115	w−	−17	125	s	73	135	w−	16	145	m	−50

TABLE IX. *Final parameter values.*

Atoms	In angular measure			In fractions of cell dimensions		
	$2\pi x$	$2\pi y$	$2\pi z$	x	y	z
K I	80°	90°	340°	0.22	0.25	0.95
K II	235°	90°	240°	0.65	0.25	0.67
S I	250°	90°	80°	0.70	0.25	0.22
S II	5°	90°	115°	0.01	0.25	0.32
O I	25°	20°	85°	0.07	0.06	0.24
O II	225°	20°	110°	0.63	0.06	0.31
O III	240°	90°	10°	0.67	0.25	0.03

In Table IX are listed the final parameter values, expressed in angular measure and in fractions of the cell dimensions.

9. DISCUSSION OF THE ATOMIC ARRANGEMENT

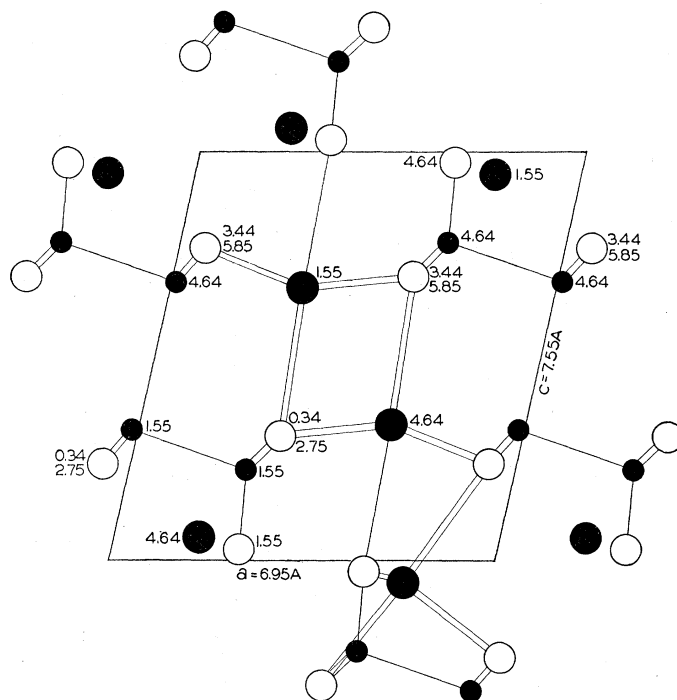A projection of the atomic arrangement on the 010 face is reproduced in Fig. 1.

Fig. 1. The atomic arrangement projected on the *b* face. Large open circles represent oxygen atoms, large filled circles represent potassium atoms and small filled circles represent sulphur atoms. The attached numbers give the heights of the atoms above the projection plane expressed in *A*. Only some of the potassium to oxygen bonds are drawn.
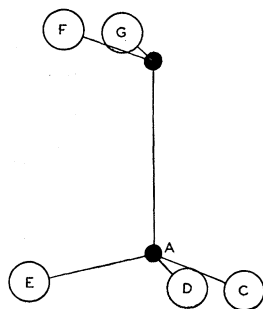

Fig. 2. The pyrosulphite group. Atoms denoted *A* and *B* are sulphur atoms, atoms denoted *CDEFG* are the oxygen atoms.

A potassium atom of the first kind (K I) is surrounded by nine oxygen atoms at approximately the same distance. There are two O I atoms at a distance of 2.88A, two O I atoms at 2.91A, two O II atoms at 3.02A, two O III

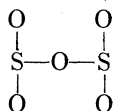atoms at 3.21A and one O III atom at 3.01A. The average distance K I − 0 is 3.01A.

A potassium atom of the second kind (K II) is surrounded by seven oxygen atoms at an average distance of 2.78A. There are two O I atoms at 2.69A, two O II atoms at 2.74A, two O II atoms at 2.95A and one O III atom at 2.71A.

The fact that the average distance K I−O is greater than the average distance K II−O is in agreement with the empirical result that the interatomic distance increases with increasing coordination number. The distances K−O calculated for cordination numbers 9 and 7 from ionic radii published by the author are 2.93A and 2.85A,[4] against the values 3.01A and 2.78A observed.

The structure found for the pyrosulphite group is of exceptional interest. A drawing of the group is reproduced in Fig. 2. We may most conveniently describe the radical as consisting of a sulphite group and a sulphur dioxide molecule with a bond between the two sulphur atoms. The structural formula consequently has to be written as

$$
\begin{array}{ccc}
O & O \\
| & | \\
O-S-S-O \\
| \\
O
\end{array}
$$
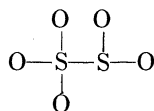
whereas the formula given by the chemists:

$$
\begin{array}{ccc}
O & & O \\
| & & | \\
S-O-S \\
| & & | \\
O & & O
\end{array}
$$

is incorrect.

The distances within the S_2O_5 group are: (the lettering referring to Fig. 2):

S I−S II	(A−B)	2.18A	O I−O I	(F−G)	2.41A
S I−O II	(A−C, A−D)	1.49A	O II−O II	(C−D)	241A
S I−O III	(A−E)	1.44A	O II−O III	(C−E, D−E)	2.49A
S II−O I	(B−F, B−G)	1.45A			

The angles between the four bonds of S I are: ($\nless BAC$ and $\nless BAD$) 105°, ($\nless CAD$) 108°, ($\nless CAE$ and $\nless DAE$) $116\frac{1}{2}$°, ($\nless BAE$) 104°.

The angles between the three bonds of S II are: ($\nless FBG$) 112°, ($\nless ABF$ and $\nless ABG$) 102°.

The closest distance between oxygen atoms belonging to different pyrosulphite groups is greater than 3.4A, in harmony with predictions made by the author.[4] A further indication of the stability of the crystal lattice is the large distance between potassium atoms and between a potassium atom and a sulphur atom.

The reason for the observed cleavage parallel to the 001 face (the $10\bar{1}$ face according to Groth's axes) is obvious from Fig. 1. There are only four potassium to oxygen bonds per 42A² of surface crossing the 001 face. The reported twinning after the $10\bar{1}$ face is due to the fact that the perpendicular to the twinning plane is a pseudo-twofold axis.

[4] W. H. Zachariasen, Zeitschr. f. Krist. **80**, 137 (1931).

The atomic arrangement is too complicated to allow a calculation of the optical properties. The acute bisectrix lies very nearly perpendicular to the connection line between sulphur atoms in the (S_2O_5) groups.

10. The Relations Between the Structure of the Pyrosulphite Group and that of Other Sulphur Oxygen Groups

The structures of the sulphate group,[5] the sulphite group[6] and the dithionate group[7] have been determined previously. The angles between the bonds are in all cases close to the tetrahedral angle ($109\frac{1}{2}°$). According to ideas presented by Pauling[8] and Slater[9] the angle between bonds which can be ascribed to p electrons tends to be $90°$. If, however, the p and s eigenfunctions have lost their individuality due to the perturbations, the angles between the bonds will tend to be $109\frac{1}{2}°$.

All the groups (S_mO_n)$^{-2}$ can be interpreted by means of single electron pair bonds. Closed shells of four electron pairs are then formed around every atom in the group. The structure of the pyrosulphite group represented in two dimensions will be.:

$$:\overset{..}{O}:$$
$$:\overset{..}{O}:\overset{..}{S}\ :\ \overset{..}{S}:\overset{..}{O}:$$
$$:\underset{..}{O}:\ :\underset{..}{O}:$$
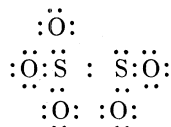
If we remove an oxygen atom in the dithionate group without altering the arrangement of the remaining atoms, we get the structure of the pyrosulphite group. In the pyrosulphite group the four atoms $ACDE$ of Fig. 2. give us an (SO_3)$^{-2}$ group of practically the same shape and dimensions as was found in the crystal lattice of Na_2SO_3. Analogously we would expect the three atoms BFG of Fig. 2 to represent the structure of the group (SO_2)$^{-2}$. The atoms AB give us an (S_2)$^{-2}$ group practically the same as found in FeS_2. Also the groups (S_2O_2)$^{-2}$, (S_2O_3)$^{-2}$ and (S_2O_4)$^{-2}$ can be represented by Fig. 2 if we remove some oxygen atoms. We do not know, however, which of the oxygen atoms we must remove. For example we can get two models for the structure of the (S_2O_3)$^{-2}$ group, either the atoms $ABCDE$ or the atoms $ABCDF$.

However, predictions of this kind need experimental verification. Investigations on the structure of other groups formed by sulphur and oxygen have been started in this laboratory.

[5] E.g., W. H. Zachariasen and G. E. Ziegler, Zeitschr. f. Krist. **81**, 92 (1931).

[6] W. H. Zachariasen and H. E. Buckley, Phys. Rev. **37**, 1295 (1931).

[7] M. L. Huggins, and Glenn O. Frank, Amer. Min. **16**, 580 (1931).

[8] L. Pauling, J. Amer. Chem. Soc. **53**, 1367 (1931).

[9] J. C. Slater, Phys. Rev. [2], **37**, 481 (1931).