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The Crystal Structure of $U(SO_4)_2 4H_2O$

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$U(SO_4)_2 4H_2O$ has an orthorhombic unit cell containing four formula units and with the dimensions

$$a = (14.674 \pm 0.005) \text{ Å}$$
$$b = (11.093 \pm 0.005) \text{ Å}$$
$$c = (5.688 \pm 0.005) \text{ Å}$$
$$V = 925.8_9 \text{ Å}^3$$

A structure is proposed with atomic positions in the space group No. 62 *Pnma*. The positions of the uranium and sulphur atoms were determined with Fourier methods. The parameters of the oxygen atoms were deduced from geometrical considerations, using interatomic distances from previously determined structures. The crystals are built up of layers parallel to the *yz* plane and formed by uranium atoms and sulphate groups. The layers are held together by water molecules, so that each sulphate tetrahedron has two oxygen atoms linked with hydrogen bonds to adjacent water molecules. Every uranium atom is in contact with four sulphate groups and four water molecules, so that the coordination of oxygen atoms around uranium is eightfold in the shape of a square Archimedean antiprism.

Uranium(IV)sulphate-tetrahydrate was first prepared by Ebelmen [1] by a photochemical reduction of U_3O_8 in the presence of ethanol and diluted sulphuric acid.

Meyer and Nachod [2] obtained the salt as a green crystalline precipitate when concentrated sulphuric acid was added slowly to a uranium(IV)-solution, keeping the temperature between 0 °C and 70 °C. The crystals formed star-shaped needles and were according to Ebelmen [1] and Kohlschütter [3] insoluble in ethanol and ether and were not reactive towards the water vapor and oxygen of the air.

The crystallographic results are summarized by Groth [4] as: orthorhombic bipyramidal, $b:a:c = 0.7563:1:0.3805$ (with the orientation of the axes in agreement with the present investigation).

PREPARATION OF THE CRYSTALS

A saturated solution of uranium(IV)sulphate in 1.0 M H_2SO_4 was prepared. When 30 ml of this solution was sealed and heated in a thick-walled glass tube (Pyrex) to 90° C in an oven for about a week, good crystals for X-ray work were obtained. (The method according to Lundgren [5]). After cooling, the glass tube was opened and the crystals were filtered off, washed with water and dried in air.

The crystals were dark green and most of them formed rather thin plates about 0.05 — 0.2 mm in length. Some crystals of more needle-shaped form were however also obtained and sometimes the crystals had grown together into clusters of varying appearance.

Analysis. A sample was dissolved in hot nitric acid (1:1) and the *uranium* was precipitated with 8-hydroxyquinoline according to Hecht and Donau [6]. The precipitate was filtered off, washed with water, ignited and weighed as U_3O_8. The amount of *sulphate* in the filtrate was determined gravimetrically by precipitation as $BaSO_4$.

The *water* was determined by Hartwig-Bendig's [7] modification of Brush [8] and Penfield's [9] method.

The *density* of the crystals was determined from the loss of weight in benzene.

	Calculated for $U(SO_4)_2 4H_2O$	Found	
% UO_2	53.77	53.9	54.0
% SO_3	31.87	32.0	31.9
% H_2O	14.36	14.2	14.0
Density	3.60	3.6_3 *	3.59

The density is calculated for 4 formula units per cell.

UNIT CELL AND SPACE GROUP

From rotation and Weissenberg photographs (zero, first and second layer), taken with CuK-radiation, of two small crystals of different shapes, (one needle rotated around the needle axis, [001], and one plate rotated around a diagonal in the plane of the plate, [010]), it was concluded that the crystals are orthorhombic and that the dimensions of the unit cell are about 14.5_5 Å, 10.9_7 Å and 5.6_4 Å.

The reflections were recorded photographically with the multiple film technique and the relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. The values of F^2 were then calculated by division with the expression $(1 + \cos^2 2\Theta)/\sin 2\Theta$.

More accurate values for the unit cell dimensions were calculated from a powder photograph, taken with monochromatized Cu$K\alpha$-radiation in a focussing camera of Guinier type, *cf.* Table 1.

$$a = (14.674 \pm 0.005) \text{ Å}$$
$$b = (11.093 \pm 0.005) \text{ Å}$$
$$c = (5.688 \pm 0.005) \text{ Å}$$
$$V = 925.8_9 \text{ Å}^3$$

The value (3.60) found for the density gives 4 formula units in the unit cell.

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* This density determination was made with small amounts of substance and thus this value is more uncertain than the second one.

The reflections systematically absent are

$$hk0 \text{ with } h = \text{odd}$$
$$0kl \text{ with } k+l = \text{odd}$$

This is characteristic of the two space groups No. 62 *Pnma* and No. 33 $Pn2_1a$. At first only the space group of higher symmetry (*Pnma*) was considered and since it was possible to find a plausible structure assuming this space group, the low-symmetrical ($Pn2_1a$) was not taken into account.

In No. 62 *Pnma* the following point positions are possible

$4(a)$: $000;\ 0\tfrac{1}{2}0;\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2};$ $4(b)$: $00\tfrac{1}{2};\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}00;\ \tfrac{1}{2}\tfrac{1}{2}0;$

$4(c)$: $\pm (x,\tfrac{1}{4},z);\ \pm (\tfrac{1}{2} + x,\tfrac{1}{4},\tfrac{1}{2}-z)$

$8(d)$: $\pm (x,y,z);\ \pm (\tfrac{1}{2} + x,\tfrac{1}{2}-y,\tfrac{1}{2}-z);\ \pm (\bar{x},\tfrac{1}{2} + y,\bar{z});\ \pm (\tfrac{1}{2}-x,\bar{y},\tfrac{1}{2} + z).$

Table 1. Powder photograph of $U(SO_4)_24H_2O$. CuKa-radiation. $\lambda_{CuKa} = 1.5418$ *Å.*

hkl	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	pF^2 calc	*I* obs	*hkl*	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	pF^2 calc	*I* obs
200	110	110	19	m	212	894	—	0	—
210	159	160	24	st	511	922	923	34	w+
020	193	192	16	m	022	928	—	0	—
101	211	211	2	v v w	122	956	954	110	v v st
011	232	231	28	s t	302	983	984	10	v v w
111	260	259	74	v v st⁻	141	984		7	
201	294	293	44	v st	600	994	995	23	w
220	304	304	18	w+	312	1032	1031	148	v v st
211	342	342	18	w+	222	1038	—	0	—
121	405	404	30	m+	610	1042	—	4	—
301	432	432	13	w	431	1060	1059	13	v v w
400	442	442	23	m	241	1067	1069	37	st
311	480	—	0	—	521			26	
221	487	488	12	v w	402	1176	—	0	—
410	490	490	40	st	322			2	—
230	545	545	90	v v st	601	1177	—	0	—
031	618	617	72	v st	620	1187	1186	45	m
401	625	625	46	v v st	132	1197	1198	41	m
321			131		341	1205	1205	74	v st
420	635	—	0	—	440	1214	1214	12	v v w
131	646	649	19	v w	412	1225	1226	0	v st
411	674	—	6	—	611	1226		77	
231	729	729	14	w	232	1280	—	0	—
002	735	—	0	—	531	1308	1309	42	m
102	762	759	9	v v w	250	1318	1317	11	v v w
040	773	772	16	w	422	1370	—	0	—
112	811	808	9	v v w	621	1371	—	1	—
421	819	822	20	w	051	1391	1391	31	m
202	845	—	0	—	441	1398	1398	20	v w
331	867	—	3	—	332	1418	1419	109	v v st
501	874	877	7	m+	151	1419		39	
430	876		34		502	1425		21	
240	883	883	8	v w	630	1428	—	0	—

The powder photograph has been measured and interpreted to $\sin^2\Theta = 0.48$.
Reflections systematically absent in space group no. 62 *Pnma* have been omitted.

POSITIONS OF THE URANIUM ATOMS

In order to find the four uranium positions, the Patterson functions $P(uvp)$ and $P(upw)$ were calculated (Figs. 1 and 2).

The four uranium atoms in the unit cell must occupy one of the fourfold positions, *i. e.* 4(a), 4(b) or 4(c). If they were situated in 4(a) or 4(b), $P(uvp)$ should have high peaks at $u = 0$, $v = \frac{1}{2}$, at $u = \frac{1}{2}$, $v = 0$, and at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $P(upw)$ should have high maxima at $u = 0$, $w = 0$, and at $u = \frac{1}{2}$, $w = \frac{1}{2}$. $P(uvp)$ has, however, no maximum at $u = 0$, $v = \frac{1}{2}$ and $P(upw)$ has no maximum at $u = \frac{1}{2}$, $w = \frac{1}{2}$. Thus the uranium atoms are situated in 4(c).

In the point position 4(c) the U—U distances would be

$$\begin{gathered} \pm\,(\tfrac{1}{2},0,\tfrac{1}{2} \pm 2z) \\ \pm\,(\tfrac{1}{2} \pm 2x,\tfrac{1}{2},\tfrac{1}{2}) \\ \pm\,(\pm\, 2x,\tfrac{1}{2},2z) \end{gathered}$$

The Patterson projections on the uv and uw plane would thus show (besides the origin maxima) the following maxima

in the uv *plane*		*in the* uw *plane*	
I. $\pm\,(\frac{1}{2},0)$	weight 4	IV. $\pm\,(\frac{1}{2},\frac{1}{2}-2z)$	weight 2
II. $\pm\,(\frac{1}{2}-2x,\frac{1}{2})$	weight 2	V. $\pm\,(\frac{1}{2}-2x,\frac{1}{2})$	weight 2
III. $\pm\,(2x,\frac{1}{2})$	weight 2	VI. $\pm\,(\pm\, 2x,\ 2z)$	weight 1

Now there are two high peaks in $P(uvp)$ at $u = 0.15_8$, $v = \frac{1}{2}$ (A in Fig. 1) and at $u = 0.34_2$; $v = \frac{1}{2}$ (B in Fig. 1) and one peak at $u = \frac{1}{2}$, $v = 0$, whose height is about double that of the other two. (All maxima have been located by the interpolation table given by Booth [10]). These maxima certainly correspond to the U—U vectors I, II, and III and if the peak A corresponds to the vector II above (and B to III) we get $x_U = 0.17_1$. However, if the peak A corresponds to the vector III (and B to II) we get $x_U = 0.07_9$. (It is sufficient to consider the range $0 \leq x \leq \frac{1}{4}$, $0 \leq z \leq \frac{1}{4}$).

The projection $P(upw)$ must have one high peak at $w = \frac{1}{2}$ (corresponding to the vector V above) and if $x_U = 0.17_1$ this maximum should be at $u = 0.15_8$ or if $x_U = 0.07_9$ at $u = 0.34_2$. Now the projection $P(upw)$ has a pronounced peak at $u = 0.15_8$, $w = \frac{1}{2}$ (C in Fig. 2) and a considerably lower maximum at $u = 0.33_1$, $w = \frac{1}{2}$ (3 in Fig. 2). Of these two peaks, the first one (C) has the correct height in comparison with the other maxima in this projection (see below) and with the calculated weights above, and thus certainly corresponds to the vector V above. (In fact, the lower peak (3) was found to correspond to a U—S vector, see p. 605). Thus we conclude $x_U = 0.17_1$.

Moreover the projection $P(upw)$ has two more peaks, one at $u = \frac{1}{2}$, $w = 0.25_4$ (D in Fig. 2) and one at $u = 0.34_2$, $w = 0.25_4$ (E in Fig. 2). If we identify the vectors IV and V with the high maxima D and C (giving the coordinates $x_U = 0.17_1$, $z_U = 0.12_3$), the projection must have one peak at

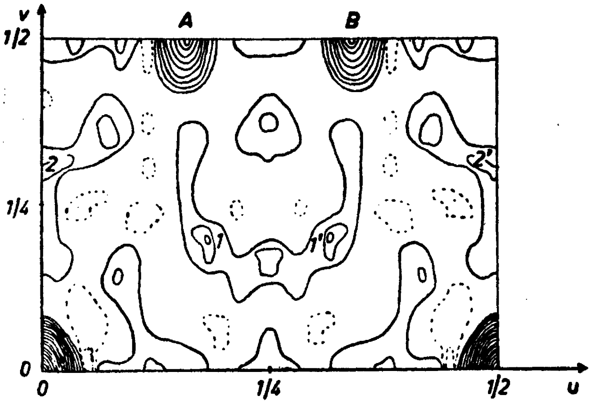

Fig. 1. The Patterson function P (uvp) for $U(SO_4)_24H_2O$. Dotted lines indicate negative values. The figures 1,1', 2 and 2' denote peaks due to U—S vectors (see text p. 602).

$u = 0.34_2$, $w = 0.25_4$ (corresponding to the vector VI above), whose height should be half that of the other two. Since the height and the position of E correspond to these calculated values we thus conclude:

4 U in No. 62 *Pnma* 4(*c*) with $x \approx 0.171$, $y = \frac{1}{4}$, $z \approx 0.123$.

POSITIONS OF THE SULPHUR ATOMS

Electron density projections. For a salt like $U(SO_4)_24H_2O$ the electron density projections could rather easily be calculated, since the signs of all the *F*-values could be determined from the contributions given by the uranium atoms, because of their dominant scattering factors. In this way, $\varrho(xyp)$ and $\varrho(xpz)$ were calculated and the results are given in Figs. 3 and 4.

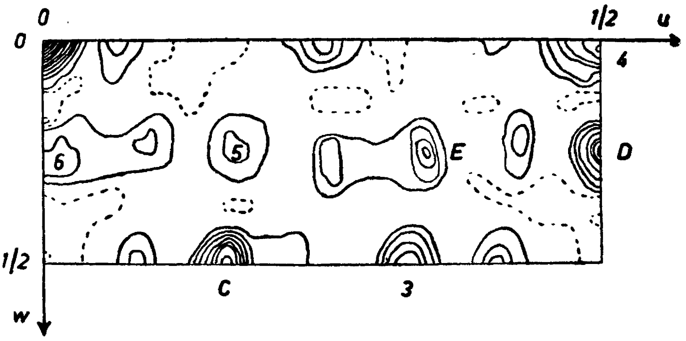

Fig. 2. The Patterson function P (upw) for $U(SO_4)_24H_2O$. Dotted lines indicate negative values. The figures 3—6 denote peaks due to U—S vectors (see text p. 602).

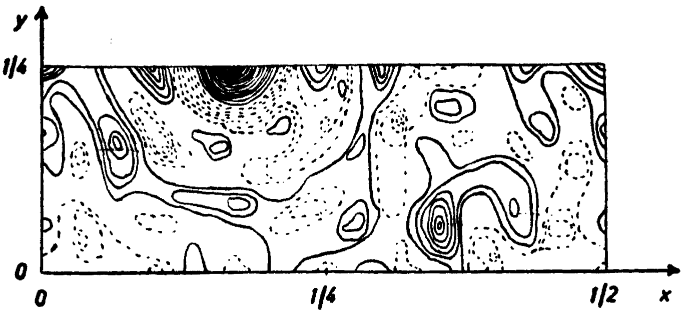

Fig. 3. Electron density of $U(SO_4)_2 4H_2O$ *projected on the* xy *plane. Dotted lines indicate negative values. In the uranium peak only every second contour has been marked out.*

From Fig. 3 we see, that there is, besides the very high maximum at $x = 0.171$, $y = 0.250$ giving the position of the uranium atom at this quadrant, a lower one at $x = 0.35$, $y = 0.05$. The electron density projected on the xz plane (Fig. 4) also shows, apart from the uranium maximum at $x = 0.171$, $z = 0.121$, a quite high peak at $x = 0.15$, $z = 0.37$. If the lower peaks in these projections are real maxima and not false formed by errors, diffraction effects or errors in the observed intensities due to absorption in the crystal [11], the only atoms, which could give peaks of this height, are the sulphur atoms.

In order to find out, if the lower maxima from $\varrho(xyp)$ and $\varrho(xpz)$ really correspond to sulphur positions in the unit cell, the uranium atoms were subtracted from the Fourier maps in Figs. 3 and 4 and thus two new electron density projections were calculated by the expressions

$$\varrho_s(xyp) = \sum_h \sum_k F_{\text{obs}(hk0)} \cdot \cos 2\pi\ (hx + ky) - \sum_h \sum_k F_{\text{U}(hk0)} \cdot \cos 2\pi\ (hx + ky)$$

$$\varrho_s(xpz) = \sum_h \sum_l F_{\text{obs}(h0l)} \cdot \cos 2\pi\ (hx + lz) - \sum_h \sum_l F_{\text{U}(h0l)} \cdot \cos 2\ (hx + lz)$$

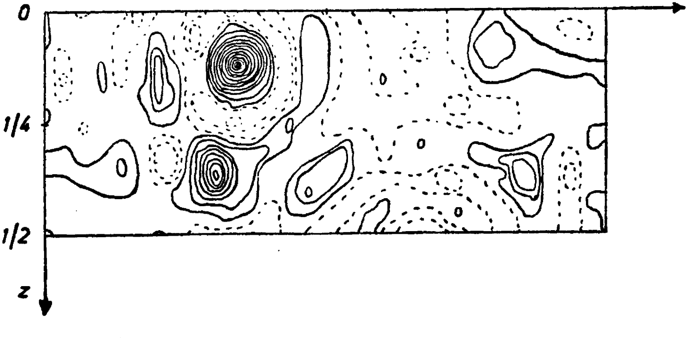

Fig. 4. Electron density of $U(SO_4)_2 4H_2O$ *projected on the* xz *plane. Dotted lines indicate negative values. In the uranium peak only every second contour has been marked out.*

In these new electron density projections, F_{obs} are the observed structure factors and F_U are the calculated uranium contributions to the structure factors normalized by multiplication

with the constant $\frac{\sum_{h,k} |F_{obs(hk0)}|}{\sum_{h,k} |F_{calc\ U(hk0)}|}$ at $\varrho_s(xyp)$ and

with the constant $\frac{\sum_{h,l} |F_{obs(h0l)}|}{\sum_{h,l} |F_{calc\ U(h0l)}|}$ at $\varrho_s(xpz)$.

The effect of the temperature factor, calculated by the ordinary procedure, was found to be negligible.

From Fig. 5, which shows $\varrho_s(xyp)$, we see that the uranium atoms have disappeared and that there is a rather distinct maximum at $x = 0.351$, $y = 0.054$, which should give the position of the sulphur atom. In the unit cell there are eight sulphur atoms and, with the parameters above, they must occupy the point position 8(*d*), if they belong to the space group No. 62 *Pnma* which was presumed, when $\varrho_s(xyp)$ was calculated. Since this projection really shows distinct maxima, this assumption seems to be very probable.

If the sulphur atoms are situated in 8(*d*), two sulphur maxima overlap in the *xz* projection of the electron density, and thus we get a ratio between the heights of the sulphur and the uranium peaks of about twice the ratio of the sulphur and uranium maxima obtained from the electron density projected on the *xy* plane. Fig. 6 shows $\varrho_s(xpz)$ and, as is seen, the uranium atom and most of its diffraction effects have disappeared, but there is, however, a pronounced maximum at $x = 0.149$, $z = 0.379$, which could be ascribed to sulphur atoms, and moreover this peak has the correct height corresponding to eight sulphur atoms in No. 62 *Pnma* 8(*d*).

Thus from the electron density projections the following set of parameters could be obtained

4 U in No. 62 *Pnma* 4(*c*) with $x = 0.171$, $y = \frac{1}{4}$, $z = 0.121$

8 S in No. 62 *Pnma* 8(*d*) with $x = 0.351$, $y = 0.054$, $z = 0.879$

Using these parameters, the U—S distances were calculated and the remaining maxima in the Patterson projections (Figs. 1—2) were compared with the U—S vectors. They were found to correspond to the maxima 1,1′, 2 and 2′ in *P*(*uvp*) and to 3, 4 and 5 and 6 in *P*(*upw*) and moreover the heights of the peaks also corresponded to the calculated weights. The remaining maxima in the Patterson projections may correspond to U—O vectors but, since the peaks due to some U—S and all U—O vectors are of about the same height as the false maxima [11], the remaining peaks were not considered.

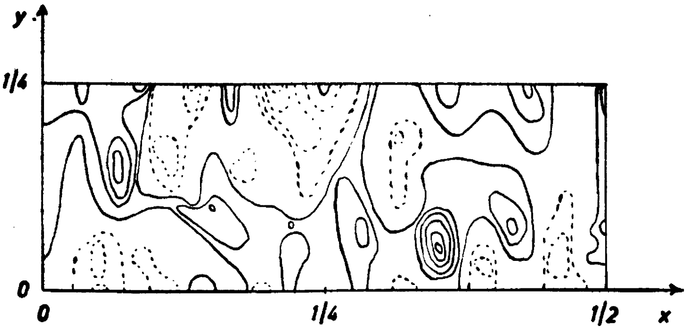

Fig. 5. Electron density of U $(SO_4)_2 4H_2O$ projected on the xy *plane and with the uranium atom substracted. Dotted lines indicate negative values.*

POSITIONS OF THE OXYGEN ATOMS

General remarks. The light hydrogen and oxygen atoms do not make any appreciable contribution to the intensities of the reflections and their positions had thus to be found from considerations of the interatomic distances. The following assumptions were then made

1. The U—O distance was assumed to be not less than that found[12–14] in UO_2, *i. e.* 2.3_6 Å.

2. The sulphate ion was considered to be a regular tetrahedron with the sulphur atom situated at its centre and with the bond lengths S—O = 1.4_7 Å and O—O = 2.4_0 Å. These distances are mean values of those published[15,16] for S—O and O—O in SO_4^{2-} and also in $S_2O_5^{2-}$ and $SO_3NH_2^-$.

3. The distance between two oxygen atoms, not belonging to the same sulphate group, was assumed to be not less than 2.6_0 Å.

With these assumptions the space free for oxygen atoms will be reduced as follows.

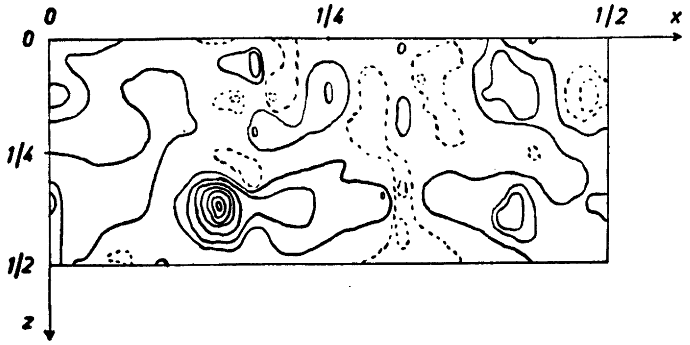

Fig. 6. Electron density of U $(SO_4)_2 4H_2O$ projected on the xz *plane and with the uranium atom subtracted. Dotted lines indicate negative values.*

There are two symmetry planes in the unit cell at $y = \pm \frac{1}{4}$. If an oxygen atom is not situated exactly in a symmetry plane, it must be at a distance of at least 1.3_0 Å from it. Accordingly, the y coordinates of the atoms should be either $y = \frac{1}{4}$ and $y = \frac{3}{4}$ or within the limits: $-0.13_3 \leq y \leq 0.13_3$, $0.36_7 \leq y \leq 0.63_3$. Moreover there are eight symmetry centres per unit cell (the point positions 4(*a*) and 4(*b*)). If an oxygen centre does not coincide with a symmetry centre, it must be situated outside a sphere of radius 1.3_0 Å around it. For the same reason spheres, of radii 2.6_0 Å around each oxygen atom which has been located and of radii 2.3_6 Å around each uranium atom, enclose domains forbidden for the centres of other oxygen atoms.

Positions of the sulphate oxygen atoms. For the sulphate oxygen atoms it seems probable that they are strongly attracted by the highly charged uranium ions. With the assumptions made above, the distance U—S should be $\leq 3.8_3$ Å, if a sulphate oxygen atom is in contact with a uranium atom. Now, in the structure found above, the uranium atoms are surrounded by four sulphur atoms at a distance of 3.6_9 Å, and each of the sulphur atoms has two uranium atoms at the same distance (Fig. 7). The angle, U—S—U, between the sulphur and the two neighbouring uranium atoms is 128°. Thus it is possible for at most two sulphate oxygen atoms, belonging to the same sulphate group, to be in contact with two different uranium atoms. Assuming this, which seems to be very probable, and regarding the sulphur positions as definite, we obtain an approximate position of the sulphate tetrahedron according to the following:

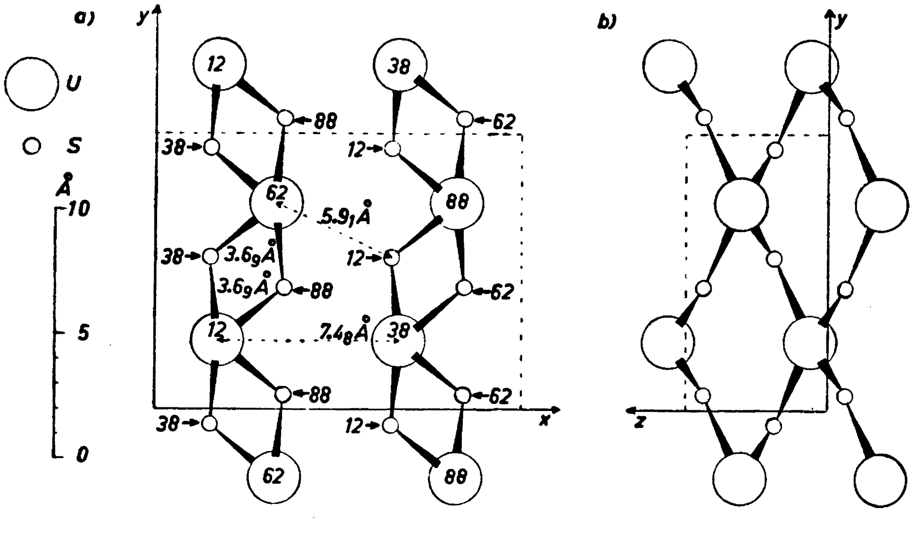

Fig. 7. Contacts (via oxygen atoms, which have not been indicated) between the uranium and the sulphate ions. a) Projection on the xy *plane. The figures denote the height of the atoms in percentages of* c. *b) Projection on the* yz *plane showing the contact in the* $U(SO_4)_2$*-layers. Only one layer has been indicated, i. e. uranium and sulphur atoms with* x *parameters between* 0 *and* $\frac{1}{2}$.

8 O_1 in 8(d) in contact with uranium; *i. e.* the oxygen centre should be situated on a circle with radius 0.5_6 Å and with the centre at $x = 0.28_4$, $y = 0.12_7$ and $z = 0.96_9$.

8 O_2 in 8 (d) in contact with uranium; *i. e.* the oxygen centre situated on a circle with radius 0.5_6 Å and with the centre at $x = 0.34_3$, $y = 0.94_1$, $z = 0.78_3$.

8 O_3 and 8 O_4 in 8(d).

However, there are 16 more oxygen atoms in the unit cell and to determine the positions of the sulphate groups more exactly, it seemed necessary at this state of the investigation to determine the positions of these non-sulphate oxygen atoms using the sulphate group position concluded above.

Positions of the non-sulphate oxygen atoms. For the non-sulphate oxygen we note, as before for the sulphate oxygen atoms, that they must be strongly attracted by the tetravalent uranium ions and consequently should be situated as close to them as possible.

Now, we have found contacts U—4O, *i. e.* four sulphate oxygen atoms in contact with each uranium, and if all of the non-sulphate oxygen atoms are in contact with uranium, we obtain the coordination U—8O. Now, in UO_2, which has CaF_2 structure[17] every uranium is surrounded by eight oxygen atoms and this is also to be expected for ions of this radius ratio[18]. It seems thus reasonable that the coordination U—8O also occurs in $U(SO_4)_2 4H_2O$ and hence we investigate the possibility that all of the non-sulphate oxygen atoms in the unit cell are in contact with uranium. This will eliminate the point positions 4(a) and 4(b) for the non-sulphate oxygen atoms and a careful survey shows that the only possibility of obtaining contact between uranium and all of the non-sulphate oxygen atoms is with

4 O_5 in 4(c)
4 O_6 in 4(c)
8 O_7 in 8(d).

Now we have to find the position of O_7. It is situated in an eightfold position and, with the assumptions made (see p. 606), reasonable interatomic distances were only obtained assuming:

8 O_7 in 8(d); $x = 0.08_3$, $y = 0.12_4$, $z = 0.87_5$.

In order to determine the x and z coordinates of O_5 and O_6 the section $y = \frac{1}{4}$ in the unit cell was drawn and domains forbidden for oxygen atoms were marked out (Fig. 8). From the figure we see that there are only two small arcs of the U—O circles, left free for the centres of O_5 and O_6. The coordinates of these oxygen atoms would then be

4 O_5 in 4(c); $x = 0.04_2$, $y = \frac{1}{4}$, $z = 0.36_8$.

4 O_6 in 4(c); $x = 0.30_0$, $y = \frac{1}{4}$, $z = 0.36_8$.

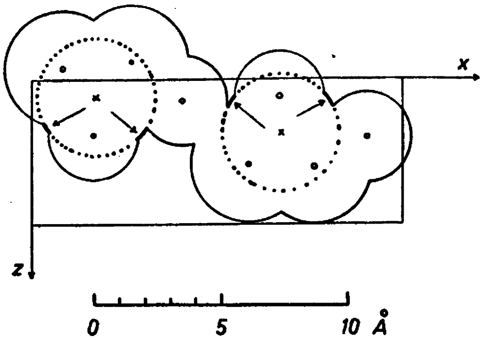

Fig. 8. Section at $y = \frac{1}{4}$ *through the unit cell showing the areas forbidden for the non-sulphate oxygen atoms* (O_5 *and* O_6) *in this plane. Thick circles indicate* $U-O$ *contacts and thin circles enclose domains forbidden around the sulphate oxygen atoms and the oxygen atoms* O_7. *The arrows point out the only arcs of the* $U-O$ *circles left free for the centres of* O_5 *and* O_6.

\+ = *centre of uranium* ○ = *centre of oxygen*

Thus for the non-sulphate oxygen atoms we conclude

4 O_5 in No. 62 *Pnma* 4(*c*) with $x = 0.04_2$, $y = \frac{1}{4}$, $z = 0.36_8$

4 O_6 in No. 62 » 4(*c*) with $x = 0.30_0$, $y = \frac{1}{4}$, $z = 0.36_8$

8 O_7 » » 62 » 8(*d*) with $x = 0.08_3$, $y = 0.12_4$, $z = 0.87_5$.

FINAL POSITIONS OF THE LIGHT ATOMS

Now, when the positions of the atoms O_5—O_7 had been determined, the parameters of the sulphate oxygen atoms could be obtained from space considerations. It was concluded above that two of the four oxygen atoms in a sulphate group are in contact with uranium. We had also found that the centres of these two oxygen atoms (O_1 and O_2) should be situated on two circles with radii and centres given above. In fact, we can get their position still more exactly, if we notice that the distance O_1—O_2 shall be 2.4_0 Å and that the y coordinates of each of the sulphate oxygen atoms shall be within the limits $-0.13_3 \leq y \leq 0.13_3$ or $0.36_7 \leq y \leq 0.63_3$. Since the parameters of the non-sulphate oxygen atoms (O_5, O_6 and O_7) are known, it is easy to determine the orientations of the regular sulphate tetrahedra so that all O—O distances (oxygen atoms not belonging to the same sulphate group) are $\geq 2.6_0$ Å and so that $U—O_1 = U—O_2 = 2.3_6$ Å. In this way the coordinates of the oxygen atoms O_1 and O_2 were obtained. Finally the positions of the remaining sulphate oxygen atoms in SO_4 tetrahedra follow immediately from the parameters for S, O_1 and O_2. Thus we obtain

8 O_1 in No. 62 *Pnma* 8(*d*) with: $x = 0.26_5$ $y = 0.12_4$ $z = 0.89$
8 O_2 » » 62 » 8(*d*) with: $x = 0.33_0$ $y = 0.92_1$ $z = 0.88$
8 O_3 » » 62 » 8(*d*) with: $x = 0.40_4$ $y = 0.08_1$ $z = 0.09$
8 O_4 » » 62 » 8(*d*) with: $x = 0.40_2$ $y = 0.08_4$ $z = 0.66$

The oxygen positions are not free from assumptions. Thus we have assumed that the oxygen atoms belong to the space group No. 62 *Pnma*, but since the uranium and sulphur atoms really belong to this group, it seems plausible to assume the same for the oxygen atoms. Moreover, the positions of the uranium and sulphur atoms cannot be far from the truth and this will make the determination of the positions of the sulphate groups rather probable. The remaining non-sulphate oxygen atoms were concluded to be in contact with uranium and the positions were obtained from space considerations. This will give a coordination figure, the square Archimedean antiprism, which is found in previously determined crystal structures of uranium salts[19-23] (see below, p. 611).

Now, there are in the unit cell four uranium atoms, eight sulphur atoms and forty-eight oxygen atoms. The signs of the structure factors were determined from the uranium contributions, but of course, the magnitudes will be influenced by the sulphur and oxygen contributions. Table 2 shows some reflections, where this influence is more pronounced and it will appear that the sulphur and the oxygen contributions lead to better agreement between observed and calculated structure factors and this is noticeable with most of the reflections, when the scattering power of these atoms was taken into account.

Table 2. Comparison between calculated and observed structure factors of some reflections from Weissenberg photographs of $U(SO_4)_2 4H_2O$ CuK-radiation.

$h\ k\ l$	F_U calc	F_S calc	$F_U + F_S$ calc	F_O calc	F calc	F obs
6 0 0	+76	+17	+93	−25	+68	67
14 0 0	−43	+12	−31	− 9	−40	43
2 1 0	−74	+ 7	−67	+18	−49	49
4 2 0	+33	−15	+18	−17	+ 1	—
4 3 0	−71	−11	−82	+24	+58	60
0 4 0	+79	+ 4	+83	−26	+57	57
2 4 0	−43	− 1	−44	+15	−29	33
2 5 0	−61	+19	−42	+ 9	−33	33
4 5 0	+64	−11	+53	+11	+64	62
0 6 0	−70	− 8	−78	−35	−113	124
4 6 0	+27	+ 7	+34	+11	+45	43
4 8 0	−24	+12	−12	+11	− 1	—
6 8 0	+58	−11	+47	− 8	+39	34
2 9 0	−49	+ 1	−48	+19	−29	35
4 9 0	+53	− 1	+52	−21	+31	34
1 0 2	−69	+18	−51	+21	−30	30
7 0 2	−64	+ 4	−60	+17	−43	42
4 0 3	+47	+ 8	+55	+13	+68	74
0 0 4	−64	−16	−80	−35	−115	116
6 1 1	−51	+ 4	−47	−15	−62	61
7 1 1	−49	− 1	−50	+14	−36	34
3 2 1	+58	+12	+70	+11	+81	71
4 2 1	−49	+ 7	−42	+10	−32	28
0 3 1	+55	+14	+69	+16	+85	86
1 3 1	+51	−11	+40	− 9	+31	27
1 6 1	−24	+ 3	−21	+ 7	−14	12

Thus it seems probable that the sulphur and oxygen coordinates concluded above are correct.

In the unit cell there are also thirty-two hydrogen atoms, which must be situated at the oxygen atoms O_5, O_6 and O_7, *i. e.* H_2O molecules. The structure would otherwise be built up of UO_2 or $U(OH)_4$ groups and neutral H_2SO_4 molecules (or HSO_4^--ions), which does not seem very probable. The hydrogen atoms may then form hydrogen bonds with the neighbouring sulphate oxygen atoms. However, it is not possible to determine the parameters of the hydrogen atoms.

FINAL STRUCTURE PROPOSITION

The following structure is thus proposed for $U(SO_4)_24H_2O$. Space group: No. 62 *Pnma*. 4 formula units per unit cell.

		x	y	z
4 U	in 4(*c*)	0.171 ± 0.003	$\frac{1}{4}$	0.121 ± 0.003
8 S	in 8(*d*)	0.351 ± 0.005	0.054 ± 0.005	$0.879 + 0.005$
8 O_1	in 8(*d*)	0.27	0.12	0.89
8 O_2	in 8(*d*)	0.33	0.92	0.88
8 O_3	in 8(*d*)	0.40	0.08	0.09
8 O_4	in 8(*d*)	0.40	0.08	0.66
4 O_5 (H_2O)	in 4(*c*)	0.04	$\frac{1}{4}$	0.37
4 O_6 (H_2O)	in 4(*c*)	0.30	$\frac{1}{4}$	0.37
8 O_7 (H_2O)	in 8(*d*)	0.08	0.12	0.88

$4(c)$: $\pm (x, \frac{1}{4}, z)$; $\pm (\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$

$8(d)$: $\pm (x, y, z)$; $\pm (\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z)$; $\pm (\bar{x}, \frac{1}{2} + y, \bar{z})$; $\pm (\frac{1}{2} - x, \bar{y}, \frac{1}{2} - z)$

The accuracy of the oxygen parameters is estimated to be about ±0.01, the z parameters being perhaps a little more uncertain. Using these parameters the structure factors for $hk0$, $hk1$ and $h0l$ were calculated and compared with the observed structure factors from the corresponding Weissenberg photographs (Table 3). Taking into account that, in spite of the choice of two crystals with different longitudinal directions, there is an absorption effect [11] in the reflections, the agreement between observed and calculated intensities is rather good.

DESCRIPTION OF THE STRUCTURE

In the structure of $U(SO_4)_24H_2O$ the uranium atoms are surrounded by eight oxygen atoms, a coordination, which is to be expected for ions of this radius ratio [18]. The coordination figure is a somewhat distorted square Archimedean antiprism, which according to Pauling [18] gives a more satisfactory ionic coordination than the cube. The same configuration around uranium is also found in $U(OH)_2SO_4$ [19] and $U_6O_4(OH)_4(SO_4)_6$ [20] and further around thorium in $Th(OH)_2CrO_4H_2O$ [21] and $Th(OH)_2SO_4$ [22] and around cerium in $CeOSO_4H_2O$ [23].

In the crystals of $U(SO_4)_24H_2O$ every uranium ion is in contact with four sulphate ions and every sulphate ions with two uranium ions, *i. e.* the crystals

Table 3. Comparison between calculated and observed structure factors from Weissenberg photographs of $U(SO_4)_2 4H_2O$. *Cu-K radiation.*

h k l	*F* calc	*F* obs
2 0 0	−62	34
4 0 0	−68	49
6 0 0	+68	67
8 0 0	−47	47
10 0 0	−22	33
12 0 0	+74	90
14 0 0	−40	43
16 0 0	−24	18
18 0 0	+39	36
2 1 0	−49	49
4 1 0	+63	50
6 1 0	−20	25
8 1 0	−67	78
10 1 0	+70	90
12 1 0	−21	31
14 1 0	−30	41
16 1 0	+51	59
18 1 0	−27	34
0 2 0	−57	66
2 2 0	+42	44
4 2 0	+ 1	—
6 2 0	−67	64
8 2 0	+47	66
10 2 0	+ 7	—
12 2 0	−42	53
14 2 0	+49	63
16 2 0	− 7	—
18 2 0	−42	44
2 3 0	+95	67
4 3 0	−58	60
6 3 0	− 5	—
8 3 0	+47	55
10 3 0	−45	50
12 3 0	+10	—
14 3 0	+45	58
16 3 0	−49	56
18 3 0	+ 6	—
0 4 0	+57	57
2 4 0	−29	33
4 4 0	−34	22
6 4 0	+76	80
8 4 0	−60	40
10 4 0	−17	—
12 4 0	+48	49
14 4 0	−32	52
16 4 0	− 4	—
18 4 0	+33	22
2 5 0	−33	33
4 5 0	+64	62
6 5 0	−29	15
8 5 0	−46	38
10 5 0	+52	48
12 5 0	−24	41
14 5 0	−25	31
16 5 0	+65	76
0 6 0	−113	124
2 6 0	+39	39
4 6 0	+45	43
6 6 0	−65	67
8 6 0	+44	33
10 6 0	+11	—
12 6 0	−57	72
14 6 0	+44	51
16 6 0	+16	—
2 7 0	+65	57
4 7 0	−58	52
6 7 0	+ 4	—
8 7 0	+63	54
10 7 0	−58	54
12 7 0	+ 6	—
14 7 0	+33	42
16 7 0	−39	32
0 8 0	+55	55
2 8 0	−32	22
4 8 0	− 1	—
6 8 0	+39	34
8 8 0	−44	34
10 8 0	− 5	—
12 8 0	+42	52
14 8 0	−43	46
2 9 0	−29	35
4 9 0	+31	34
6 9 0	− 3	—
8 9 0	−29	24
10 9 0	+50	43
12 9 0	−23	20
14 9 0	−32	27
0 10 0	−69	60
2 10 0	+35	34
4 10 0	+30	22
6 10 0	−66	52
8 10 0	+33	32
10 10 0	+27	18
12 10 0	−42	50
2 11 0	+36	34
4 11 0	−49	40
6 11 0	+17	—
8 11 0	+39	34
10 11 0	−42	43
0 12 0	+50	48
2 12 0	−32	24
4 12 0	−22	15
6 12 0	+47	42
8 12 0	−39	31
10 12 0	+ 2	—
2 13 0	−36	48
4 13 0	+53	43
6 13 0	− 3	—
0 14 0	−44	38
2 14 0	+25	17
4 14 0	+13	—
1 0 1	+14	17
2 0 1	−66	70
3 0 1	−36	34
4 0 1	+68	76
5 0 1	+26	30
6 0 1	+ 6	—
7 0 1	− 1	—
8 0 1	−54	62
9 0 1	−38	38
10 0 1	+36	39
11 0 1	+45	46
12 0 1	− 1	—
13 0 1	− 4	—
14 0 1	−32	36
15 0 1	−25	31
16 0 1	+39	42
17 0 1	+31	37
18 0 1	− 9	—
0 0 2	+ 5	—
1 0 2	−30	30
2 0 2	− 4	—
3 0 2	−31	30
4 0 2	− 1	—
5 0 2	+46	43
6 0 2	+ 4	—
7 0 2	−43	42
8 0 2	− 1	—
9 0 2	+34	33
10 0 2	− 3	—

Table 3.
(cont.)

h k l	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs
11 0 2	+17	17	10 0 5	−27	33	9 2 1	+51	57
12 0 2	+ 4	—	11 0 5	−34	31	10 2 1	−36	46
13 0 2	−61	67	12 0 5	+ 5	—	11 2 1	−31	37
14 0 2	− 1	—	13 0 5	+ 3	—	12 2 1	+18	22
15 0 2	+31	48				13 2 1	−15	—
16 0 2	− 1	—	0 0 6	−10	—	14 2 1	+18	22
17 0 2	+29	31	1 0 6	+23	31	15 2 1	+33	41
18 0 2	+ 2	—	2 0 6	+ 6	—	16 2 1	−39	50
			3 0 6	− 7	—	17 2 1	−22	23
1 0 3	−20	24	4 0 6	+ 3	—	18 2 1	+20	21
2 0 3	−52	54	5 0 6	−30	29			
3 0 3	+33	48	6 0 6	− 8	—	0 3 1	+85	86
4 0 3	+68	74	7 0 6	+38	33	1 3 1	+31	27
5 0 3	−14	12	8 0 6	+ 3	—	2 3 1	−26	27
6 0 3	− 6	—	9 0 6	−20	12	3 3 1	−13	—
7 0 3	+ 4	—	10 0 6	+ 7	—	4 3 1	−25	25
8 0 3	−57	68	11 0 6	−18	12	5 3 1	−46	36
9 0 3	+26	24				6 3 1	+43	36
10 0 3	+35	33	1 0 7	+12	12	7 3 1	+52	38
11 0 3	−42	42	2 0 7	+37	24	8 3 1	−27	26
12 0 3	+ 3	—	3 0 7	−21	20	9 3 1	−17	13
13 0 3	+ 3	—	4 0 7	−48	36	10 3 1	−17	15
14 0 3	−29	33	5 0 7	+10	12	11 3 1	−24	16
15 0 3	+25	38	6 0 7	+ 5	—	12 3 1	+36	49
16 0 3	+39	38				13 3 1	+43	54
17 0 3	−26	26	0 1 1	−53	49	14 3 1	−21	21
			1 1 1	−61	57	15 3 1	−25	36
0 0 4	−115	116	2 1 1	+30	31	16 3 1	−10	—
1 0 4	+ 9	—	3 1 1	+ 2	—	17 3 1	−19	21
2 0 4	+42	43	4 1 1	+17	—	18 3 1	+22	21
3 0 4	0	—	5 1 1	+41	36			
4 0 4	+47	44	6 1 1	−62	61	1 4 1	+19	19
5 0 4	+ 4	—	7 1 1	−36	34	2 4 1	−43	44
6 0 4	−61	53	8 1 1	+40	51	3 4 1	−61	50
7 0 4	− 8	—	9 1 1	+ 9	—	4 4 1	+32	37
8 0 4	+37	38	10 1 1	+ 8	—	5 4 1	+42	36
9 0 4	+ 3	—	11 1 1	+37	42	6 4 1	+ 2	—
10 0 4	+23	28	12 1 1	−32	36	7 4 1	+13	10
11 0 4	+ 2	—	13 1 1	−40	50	8 4 1	−38	39
12 0 4	−59	60	14 1 1	+34	44	9 4 1	−38	40
13 0 4	− 4	—	15 1 1	+ 8	—	10 4 1	+41	47
14 0 4	+32	29	16 1 1	0	—	11 4 1	+30	31
15 0 4	+ 3	—	17 1 1	+18	17	12 4 1	−11	—
			18 1 1	−31	31	13 4 1	+ 5	—
1 0 5	− 9	—				14 4 1	−22	30
2 0 5	+43	38	1 2 1	−39	43	15 4 1	−36	39
3 0 5	+29	17	2 2 1	+24	31	16 4 1	+28	30
4 0 5	−35	38	3 2 1	+81	71	17 4 1	+35	33
5 0 5	−27	29	4 2 1	−32	28	18 4 1	−12	—
6 0 5	− 1	—	5 2 1	−36	31			
7 0 5	− 4	—	6 2 1	+ 8	14	0 5 1	−56	67
8 0 5	+32	39	7 2 1	−26	23	1 5 1	−44	52
9 0 5	+36	31	8 2 1	+28	31	2 5 1	+27	31

Table 3.
(cont.)

h k l	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs
3 5 1	−2	—	11 7 1	−24	22	6 10 1	−2	—
4 5 1	+6	—	12 7 1	+30.	37	7 10 1	−3	—
5 5 1	+57	56	13 7 1	+39	39	8 10 1	+36	29
6 5 1	−35	37	14 7 1	−23	18	9 10 1	+29	27
7 5 1	−44	39	15 7 1	−16	15	10 10 1	−30	31
8 5 1	+38	40	16 7 1	−6	—	11 10 1	−33	28
9 5 1	+1	—				12 10 1	+1	—
10 5 1	+1	—	1 8 1	+32	41	13 10 1	+1	—
11 5 1	+33	44	2 8 1	−17	29			
12 5 1	−35	54	3 8 1	−59	56	0 11 1	+41	37
13 5 1	−32	52	4 8 1	+33	21	1 11 1	+31	31
14 5 1	+36	53	5 8 1	+22	16	2 11 1	−20	16
15 5 1	+4	—	6 8 1	−10	12	3 11 1	0	—
16 5 1	−3	—	7 8 1	+21	12	4 11 1	−9	—
17 5 1	+21	20	8 8 1	−21	16	5 11 1	−37	29
			9 8 1	−46	45	6 11 1	+29	20
1 6 1	−14	12	10 8 1	+27	21	7 11 1	+32	19
2 6 1	+49	54	11 8 1	+31	20	8 11 1	−28	15
3 6 1	+41	36	12 8 1	−15	19	9 11 1	−4	—
4 6 1	−44	48	13 8 1	+14	12	10 11 1	−4	—
5 6 1	−30	32	14 8 1	−16	15	11 11 1	−24	17
6 6 1	−1	—	15 8 1	−28	19			
7 6 1	−8	—				1 12 1	+15	—
8 6 1	+40	42	0 9 1	−36	38	2 12 1	−27	19
9 6 1	+34	38	1 9 1	−42	38	3 12 1	−41	32
10 6 1	−39	39	2 9 1	+18	22	4 12 1	+23	18
11 6 1	−30	31	3 9 1	+5	—	5 12 1	+25	18
12 6 1	+9	—	4 9 1	+14	—	6 12 1	−4	—
13 6 1	−1	—	5 9 1	+34	31	7 12 1	+16	9
14 6 1	+26	27	6 9 1	−37	31	8 12 1	−22	25
15 6 1	+26	29	7 9 1	−36	31	9 12 1	−31	23
16 6 1	−35	31	8 9 1	+25	16			
			9 9 1	+8	—	0 13 1	−46	36
0 7 1	+52	46	10 9 1	+5	—	1 13 1	−19	11
1 7 1	+36	32	11 9 1	+31	27	2 13 1	+22	11
2 7 1	−27	19	12 9 1	−24	24	3 13 1	+6	—
3 7 1	−6	—	13 9 1	−37	29	4 13 1	+17	10
4 7 1	−23	20	14 9 1	+27	22	5 13 1	+22	19
5 7 1	−23	15				6 13 1	−37	29
6 7 1	+56	47	1 10 1	−12	—	7 13 1	−29	26
7 7 1	+30	31	2 10 1	+37	22			
8 7 1	−28	22	3 10 1	+33	22			
9 7 1	−14	15	4 10 1	−36	31	1 14 1	−17	10
10 7 1	−17	22	5 10 1	−26	22	2 14 1	+24	—

are built up of $U(SO_4)_2$-layers parallel with the *yz* plane (Fig. 7 b). Between these layers there is water of crystallization, so that every uranium atom is in contact with four water molecules and each of them is in contact with one uranium atom. The two sulphate oxygen atoms (O_3 and O_4), which are not bound to uranium, are in contact with the water oxygen atoms (O_5, O_6 and O_7). These O—O distances vary between 2.7 and 2.9 Å, and are similar to

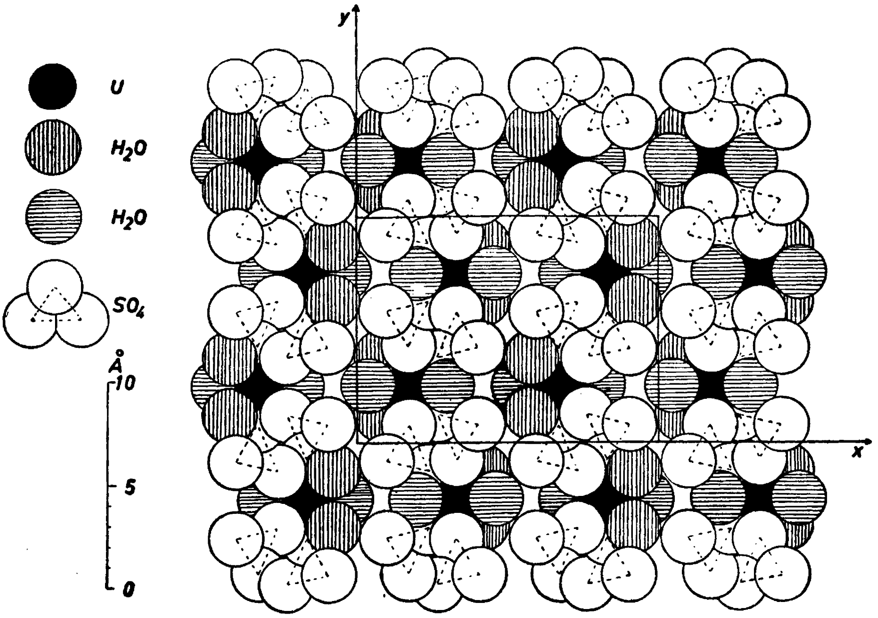

Fig. 9. Projection on the xy *plane of the structure of $U(SO_4)_2 4H_2O$.*

those found in several hydrates of oxy-salts containing O—H—O-bonds[24]. It seems therefore very probable that the layers, mentioned above, are joined by hydrogen bonds between the water oxygen atoms and the sulphate oxygen atoms O_3 and O_4.

The *xy* projection of the structure is shown in Fig. 9.

The distances U—O, S—O and O—O (within a sulphate group) were assumed to be 2.3_6 Å, 1.4_7 Å and 2.4_0 Å. The distances between the oxygen atoms, not belonging to the same sulphate group, will be (in Å)

$O_1-O_1 = 2.8_9$
$O_1-2O_2;\ O_2-2O_1 = 2 \times 3.1_5;\ 2 \times 3.2_5$
$O_1-2O_6;\ O_6-4O_1 = 3 \times 3.1_3;\ 3 \times 3.3_0$
$O_1-O_7;\ O_7-O_1 = 2.6_7$
$O_2-O_5;\ O_5-2O_2 = 2.7_7$
$O_2-O_6;\ O_6-2O_2 = 2.7_9$
$O_2-2O_7;\ O_7-2O_2 = 2 \times 3.1_6;\ 2 \times 3.1_5$
$O_3-O_4 = 3.2_3$

$O_3-O_5;\ O_5-2O_3 = 2.7_7$
$O_3-O_6;\ O_6-2O_3 = 2.8_8$
$O_3-O_7;\ O_7-O_3 = 2.7_9$
$O_4-O_6;\ O_6-2O_4 = 2.9_0$
$O_4-O_7;\ O_7-2O_4 = 2 \times 2.7_0$
$O_5-4O_7;\ O_7-2O_5 = 3 \times 3.1_9;\ 3 \times 3.2_6$
$O_7-O_7 = 2.7_9$

The O—O distances are all within the normal range, showing that the lattice is also supported by O—O contacts. However, they may be in error by a few tenths of an Ångström unit.

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