

It is obvious that experimental curves  $I_{H_1H_2}(z)$  deduced from powder diffraction patterns will be rather inaccurate except in the regions corresponding to large values of  $J_{H_1H_2}(\theta)$ , i.e. in the immediate neighborhood of the prominent diffraction maxima. To a first approximation the height of the maxima  $J_{H_1H_2}(\theta)$  is inversely proportional and the width directly proportional to the corresponding  $z$  values. Hence, the experimental error in the  $I_{H_1H_2}$  curves increases with  $z$ . It should further be noted that powder diffraction patterns will give only mean curves  $\frac{1}{2}\{I_{H_1H_2}(z) + I_{H_2H_1}(z)\}$ .

Experimental curves  $\frac{1}{2}\{I_{10}(z) + I_{01}(z)\}$  for two typical specimens of  $\text{UO}_2\text{F}_2$  are shown in Figs. 3 and 4. The curve of Fig. 3 obviously corresponds to the sample with the greater, that of Fig. 4 to the sample with the

smaller amount of stacking disorder. In the former sample one would estimate  $p_1 = 0.60-0.65$  and in the latter  $p_1 = 0.90-0.95$ .

Considering the inaccuracy of the experimental data the agreement between observed and calculated  $I_{H_1H_2}$  curves must be characterized as surprisingly good. The postulated nature of the stacking disorder can thus be said to be completely confirmed by the observations. The results outlined above have further demonstrated the value and the usefulness of the general theory of X-ray diffraction in crystals with stacking disorder.

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*Acta Cryst.* (1948). **1**, 281

## Crystal Chemical Studies of the 5f-Series of Elements. IV. The Crystal Structure of $\text{Ca}(\text{UO}_2)\text{O}_2$ and $\text{Sr}(\text{UO}_2)\text{O}_2$

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(Received 20 August 1948)

$\text{Ca}(\text{UO}_2)\text{O}_2$  and  $\text{Sr}(\text{UO}_2)\text{O}_2$  are rhombohedral and isostructural. The unit cell containing one molecule has dimensions:

$$\begin{aligned} \text{Ca}(\text{UO}_2)\text{O}_2: & \quad a = 6.254 \pm 0.001 \text{ kX.}, \quad \alpha = 36^\circ 2' \pm 1', \\ \text{Sr}(\text{UO}_2)\text{O}_2: & \quad a = 6.53 \pm 0.03 \text{ kX.}, \quad \alpha = 35^\circ 32' \pm 20'. \end{aligned}$$

The calculated density is  $7.45 \text{ g.cm.}^{-3}$  for the calcium compound and  $7.62 \text{ g.cm.}^{-3}$  for the strontium compound. The space group is  $R\bar{3}m$  with 1 U in (0, 0, 0), 1 Ca (or Sr) in  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ,  $2\text{O}_I$  in  $\pm(u, u, u)$ ,  $2\text{O}_{II}$  in  $\pm(v, v, v)$ . For the calcium compound  $u = 0.109 \pm 0.006$ ,  $v = 0.361 \pm 0.006$ .

The structure contains collinear uranyl groups with  $\text{U}-\text{O}_I = 1.91 \pm 0.10 \text{ \AA}$ . Each uranium atom forms six weaker bonds with  $\text{U}-\text{O}_{II} = 2.29 \text{ \AA}$ . A calcium or strontium atom is bonded to eight oxygen atoms with  $\text{Ca}-\text{O} = 2.45 \text{ \AA}$ ,  $\text{Sr}-\text{O} = 2.58 \text{ \AA}$ .

### Introduction

While working in the Manhattan Project during the war the writer prepared a number of uranates and studied their crystal structures in order to get information on the crystal chemistry of hexavalent uranium compounds. This article gives the results of the crystal structure investigation of calcium uranate and of the isostructural strontium uranate. These results were obtained in 1944 and presented in the classified reports of the Manhattan Projects. The structure and dimensions of the uranyl group in calcium uranate given in this paper were reported at the International Crystallographic Conference in London in 1946; but the details of the investigation have only recently been declassified. The crystal structure of the uranates was determined on the basis of the photographic data of Table 4. The spectrometer data of Tables 1-3 were taken later and

led to a complete confirmation of the structure originally found.

### The experimental data

The compounds were prepared by the writer by adding  $\text{U}_3\text{O}_8$  or  $\text{UO}_3$  to an excess of molten  $\text{CaCl}_2$  or  $\text{SrCl}_2$ . The melt was held at  $1000^\circ \text{C}$ . for half an hour, and the uranate formed as a surface crust. Both uranate preparations were of yellow-green color and consisted of microscopic crystals. These were very thin flakes with hexagonal outline and optically uniaxial character. Because of the pressure of war work it was not at the time possible to get a direct chemical analysis of the preparations. The chemical identity was therefore determined from the X-ray diffraction results as described below.

The microscopic crystals were too small to permit the use of single-crystal X-ray diffraction patterns. As a consequence crystal powder specimens were used. The

observations were taken with Cu *K* radiation filtered through nickel foil. Photographic as well as spectrometer observations were made for calcium uranate; only photographic measurements for the strontium compound. The photographic data were obtained using cylindrical specimens, while the flat briquet focusing technique was used for the spectrometer measurements. Because the crystallites were thin flakes, random orientation of crystallites was not attained in any of the specimens. As a consequence the reflections from lattice planes making small angles with the crystal flakes appeared with enhanced intensity.

Table 1. *Spectrometer data for calcium uranate*

<i>I</i>	Observed $\sin^2 \theta$	$H_1H_2H_3$	Calculated $\sin^2 \theta$
264	0.0177	111	0.0173
57	0.0549	100	0.0545
134	0.0608	110	0.0603
200	0.0698	222	0.0693
72	0.0840	211	0.0834
35	0.1012	221	0.1007
26	0.1477	322	0.1469
54	0.1561	333	0.1561
56	0.1581	110	0.1578
128	0.1759	{210	0.1751
		{332	0.1757
13	0.2132	111	0.2123
29	0.2186	200	0.2181
59	0.2277	321	0.2271
17	0.2417	220	0.2412
48	0.2455	433	0.2450
8	0.2580	311	0.2585
24	0.2769	444	0.2771
19	0.2851	443	0.2852
5	0.3046	331	0.3047
23	0.3135	432	0.3136
18	0.3331	422	0.3335
9	0.3706	201	0.3701
24	0.3757	{211	0.3759
		{544	0.3778
12	0.3986	310	0.3989
12	0.4020	442	0.4028
6	0.4149	320	0.4163
20	0.4287	554	0.4297
4	0.4313	555	0.4329
21	0.4338	543	0.4349
6	0.4430	533	0.4432
6	0.4608	421	0.4625
7	0.4712	211	0.4734

The extent of the departure from random orientation was different for the different specimens. The spectrometer data of Table 1 contain all reflections up to  $\sin^2 \theta = 0.475$ . The orientation effect was considerable in the specimen with which these data were obtained. In reducing the observed intensities to structure factors it was accordingly necessary to apply a correction. The following intensity formula was used for the data of Table 1:

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} P, \quad (1)$$

where *p* is the multiplicity of the reflecting plane and *P* the correction factor for the orientation effect. Formula (1) with *P* constant gives the structure factors listed in column 2 of Table 2, while the structure factors in the third column are obtained with

$$P = 1 + ae^{-(\alpha/\alpha_0)^2}, \quad (2)$$

setting  $a = 4.5$  and  $\alpha_0 = \pi/6$ .  $\alpha$  is the angle (in radians) between the plane of the crystal flake and the reflecting plane. It should be pointed out that (2) is an approximate rather than an exact expression for the correction factor.

Table 2. *Observed and calculated structure factors for calcium uranate*

$H_1H_2H_3$	Observed		Calculated	
	Not corrected	Corrected	U alone	U, Ca, O
111	114	43	87	75
100	57	57	81	68
110	91	90	80	96
222	211	91	79	94
211	80	71	78	73
221	62	51	76	54
322	67	48	73	50
333	173	74	72	70
110	(102)	102	72	102
111	59	59	68	58
200	89	89	68	80
321	92	86	67	78
220	73	72	66	65
433	123	72	66	77
311	52	51	65	50
444	164	70	64	71
443	86	46	64	63
331	46	41	63	47
432	71	59	63	60
422	92	82	62	80
201	48	48	60	51
310	57	57	59	59
442	81	67	59	68
320	41	41	58	45
554	108	56	58	67
555	84	36	57	40
543	79	57	57	64
533	59	47	57	55
421	42	42	56	42
211	66	66	56	75

It proved possible to prepare one specimen in which the crystal flakes were in nearly perfect alignment. As regards reflections from the lattice planes parallel to the crystal flakes this specimen is equivalent to a single crystal of mosaic type. The data obtained with this specimen are shown in Table 3. In reducing the observations to structure factors one must accordingly use the formula

$$I = \frac{I'}{1 - bI'} \propto |F|^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta}. \quad (3)$$

In this expression *I'* is the actually measured integrated intensity and *I* the intensity corrected for secondary extinction. The structure factors listed in column 4 of Table 3 were obtained from (3) with  $b = 0.0070$ .

Table 3. *Reflections ( $H_1H_2H_3$ ) for calcium uranate*

$H_1H_2H_3$	<i>I'</i>	<i>I</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	
				U alone	U, Ca, O
111	68.8	132.4	63	87	76
222	68.8	132.4	92	79	94
333	33.6	43.9	69	72	69
444	25.1	30.5	71	64	68
555	5.4	5.6	35	57	41

The orientation effect was smallest for the cylindrical specimen used for the photographic data. It was found that the correction was negligible except for reflections from planes nearly parallel to the crystal flake. The photographic data listed in Table 4 do not represent all diffraction lines. All diffraction lines which correspond to superimposed reflections or to reflections from planes making angles of less than  $39^\circ$  with the crystallite plate have been omitted from Table 4. In comparing observed and calculated intensities the expression

$$I \propto |F|^2 p \quad (4)$$

was used. Because of the very high absorption coefficient the product of absorption factor, Lorentz polarization factor and temperature factor is approximately constant. Accordingly (4) may be used if only neighboring reflections are compared.

Table 4. *Photographic data for calcium uranate*

$H_1 H_2 H_3$	$\sin^2 \theta$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	
			U alone	U, Ca, O
100	0.0563	<i>m</i> —	66	46
110	0.0615	<i>s</i>	64	91
211	0.0850	<i>m</i> —	61	53
221	0.1021	<i>w</i>	58	30
10 $\bar{1}$	0.1602	<i>m</i>	52	104
11 $\bar{1}$	0.2144	<i>w</i> —	46	33
200	0.2203	<i>w</i>	46	63
321	0.2294	<i>m</i> +	90	122
220	0.2431	<i>vw</i> +	45	42
311	0.2608	<i>w</i> —	42	25
331	0.3072	<i>vw</i>	40	22
432	0.3163	<i>w</i> +	80	72
422	0.3356	<i>w</i> +	39	64
20 $\bar{1}$	0.3725	<i>w</i> —	72	52
310	0.4015	<i>w</i>	70	65
442	0.4043	<i>w</i>	35	45
320	0.4194	<i>w</i> —	67	40
533	0.4451	<i>vw</i>	32	30
421	0.4649	<i>w</i> —	63	35
11 $\bar{2}$	0.4759	<i>w</i>	31	56
553	0.5366	<i>vwv</i>	29	14
532	0.5620	<i>w</i>	56	76
542	0.6028	<i>w</i> —	56	51
31 $\bar{1}$	0.6502	<i>vw</i>	52	37
21 $\bar{2}$	0.6871	<i>vw</i>	50	37
32 $\bar{1}$	0.7154	<i>w</i> —	50	52
410	0.7332	<i>vw</i>	49	30
521	0.8073	<i>w</i>	46	73
31 $\bar{1}$	0.8446	<i>vwv</i>	23	17
400	0.8733	<i>vw</i> —	23	25
541	0.8767	<i>w</i> +	46	60
33 $\bar{1}$	0.8901	<i>vwv</i>	23	15
642	0.9090	<i>w</i> +	46	56

#### Determination of the crystal structure

The observed sine squares correspond to a rhombohedral translation group. The unit-cell dimensions as determined from observations in the back reflection region are

$$a = 6.254 \pm 0.001 \text{ kX.}, \quad \alpha = 36^\circ 2' \pm 1'$$

The corresponding values for the strontium compound are

$$a = 6.53 \pm 0.03 \text{ kX.}, \quad \alpha = 35^\circ 32' \pm 20'$$

All reflections compatible with the unit cell given above are observed, and it is seen that the structure

factor to a first approximation is the same for all reflections. These observations require but one uranium atom per unit cell, and we shall choose the origin in this atom.

The writer has shown on the basis of extensive experimental data that each oxygen atom in uranium compounds requires a space of  $19 \pm 2 \text{ \AA}^3$ . The corresponding value is  $5 \text{ \AA}^3$  for calcium and negligible for uranium. The only formula compatible with the observed unit-cell volume of  $76 \text{ \AA}^3$  is thus  $\text{CaUO}_4$ . The calculated densities are  $\rho = 7.45 \text{ g.cm.}^{-3}$  for  $\text{CaUO}_4$  and  $\rho = 7.62 \text{ g.cm.}^{-3}$  for  $\text{SrUO}_4$ .

The next to the last column in Tables 2, 3 and 4 contains the structure factors or intensities calculated on the basis of the uranium atoms only. Comparison with observations shows that the oxygen and calcium atoms have a considerable effect on the intensities. It is seen

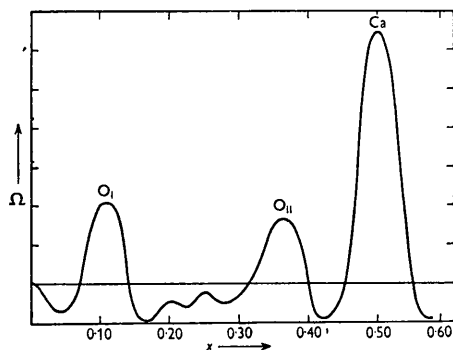


Fig. 1. The electron-density distribution along the axis ( $x, x, x$ ) due to calcium and oxygen atoms.

further that the oxygen and calcium contribution (except for the decrease with increasing scattering angle) depends only upon the linear combination  $H_1 + H_2 + H_3$ . This shows that all the oxygen atoms as well as the calcium atom must be situated on the threefold axis, i.e. at positions  $(x, x, x)$ .

The electron density along the threefold axis is given by

$$\Omega(x) \propto \sum_K A_K \cos 2\pi Kx, \quad (5)$$

where  $K \equiv H_1 + H_2 + H_3$  and where  $A_K$  is the mean structure factor for a given  $K$ . Since we are interested only in the calcium and oxygen positions, we shall set

$$A_K = (F - f_U)_K. \quad (6)$$

This procedure serves to eliminate the uranium peaks from the function  $\Omega(x)$ .

The observations lead to the following values for  $A_K$ :

$K =$	0	1	2	3	4	5
$A_K =$	+20	-15	+15	-10	0	-20
$K =$	6	7	8	9	10	
$A_K =$	+10	-20	+20	0	+10	0

Fig. 1 shows the function  $\Omega(x)$ . The large maximum at  $x = 0.50$  is evidently to be ascribed to calcium and the maxima at  $x = 0.11$  and  $x = 0.36$  to oxygen atoms. The

identification of the calcium peak is confirmed by the fact that in the  $\text{SrUO}_4$  diffraction pattern all reflections with odd  $K$  appear with greatly reduced intensity. Since there are only two oxygen maxima in the range  $0 < x < \frac{1}{2}$  there are two sets of oxygen atoms in positions  $\pm(x, x, x)$ . Considerations based upon reflections with high values of  $K$  permit a fairly accurate determination of the oxygen parameters.

The structure of  $\text{CaUO}_4$  is thus as follows:

Space group:  $R\bar{3}m$ .

Atomic positions: 1 U in  $(0, 0, 0)$ , 1 Ca in  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ,  $2\text{O}_I$  in  $\pm(u, u, u)$  with  $u=0.109 \pm 0.006$ ;  $2\text{O}_{II}$  in  $\pm(v, v, v)$  with  $v=0.361 \pm 0.006$ .

The corresponding parameter values for  $\text{SrUO}_4$  are  $u=0.104$ ,  $v=0.357$ . The parameter  $u$  was chosen so as to give the same  $\text{U}-\text{O}_I$  distance as for the calcium compound.

### Discussion of the structure

The interatomic distances in the calcium uranate structure are:

$$\begin{aligned} \text{Ca}-6\text{O}_I &= 2.45 \pm 0.05 \text{ \AA.}, & \text{U}-2\text{O}_I &= 1.91 \pm 0.10 \text{ \AA.}, \\ \text{Ca}-2\text{O}_{II} &= 2.44 \pm 0.10 \text{ \AA.}, & \text{U}-6\text{O}_{II} &= 2.29 \pm 0.02 \text{ \AA.} \end{aligned}$$

In the strontium compound the oxygen parameters were chosen so as to give the following distances:

$$\begin{aligned} \text{Sr}-6\text{O}_I &= 2.57 \text{ \AA.}, & \text{U}-2\text{O}_I &= 1.91 \text{ \AA.}, \\ \text{Sr}-2\text{O}_{II} &= 2.61 \text{ \AA.}, & \text{U}-6\text{O}_{II} &= 2.33 \text{ \AA.} \end{aligned}$$

The results for calcium uranate show that the  $\text{U}-\text{O}_I$  bonds are much stronger than the  $\text{U}-\text{O}_{II}$  bonds. There is, in other words, direct evidence for the existence of linear uranyl groups  $(\text{O}_I-\text{U}-\text{O}_I)^{+2}$  in the structure. Accordingly the chemical formulas of the compounds under investigation should be written as  $\text{Ca}(\text{UO}_2)\text{O}_2$  and  $\text{Sr}(\text{UO}_2)\text{O}_2$ .

The collinear structure of the uranyl group was first demonstrated by Fankuchen (1935) in his study of sodium uranyl acetate. He estimated a value of  $2.2 \pm 0.4$  \AA. for the  $\text{U}-\text{O}$  distance within the uranyl group. The value  $\text{U}-\text{O}_I=1.91 \pm 0.10$  \AA. found in the present paper seems to be the first reasonably reliable result for the dimensions of the uranyl group.

The binding within the uranyl group is undoubtedly of covalent type. Uranium probably forms double bonds with the  $\text{O}_I$  atoms. On this assumption the single-bond covalent radius of uranium becomes 1.43 \AA. if the oxygen single bond radius is taken as 0.66 \AA. (Huggins, 1926) or 1.35 \AA. if the value 0.74 \AA. (Schomaker & Stevenson, 1941) is used for the oxygen radius.

In addition to the two uranyl bonds, each uranium atom forms six weaker bonds with the  $\text{O}_{II}$  atoms. If one assumes that a uranium atom has six bonding electrons, each of these six secondary bonds would have a strength of  $\frac{1}{3}$  (Pauling, 1947). The  $\text{U}-\text{O}_{II}$  distance calculated on this basis is 2.38 \AA., while the observed

value is 2.29 \AA. This difference may be due to the partially ionic character of the  $\text{U}-\text{O}_{II}$  bonds.

Each calcium or strontium atom is bonded to eight oxygen atoms with mean values  $\text{Ca}-\text{O}=2.45$  \AA. and  $\text{Sr}-\text{O}=2.58$  \AA. These distances are 0.03–0.05 \AA. greater than the observed distances in  $\text{CaO}$  and  $\text{SrO}$  where the co-ordination number is six.

The  $\text{Ca}(\text{UO}_2)\text{O}_2$  structure can be regarded as an appreciably deformed  $\text{CaF}_2$  type of structure. This relationship is best illustrated by referring the latter structure to a rhombohedral cell containing two molecules. The rhombohedral angle and the atomic positions of this cell are similar to the corresponding quantities for the  $\text{Ca}(\text{UO}_2)\text{O}_2$  structure, as the following comparison shows:

$\text{Ca}_2\text{F}_4$ $\alpha = 33^\circ 14'$	$\text{Ca}(\text{UO}_2)\text{O}_2$ $\alpha = 36^\circ 2'$
1 Ca in $(0, 0, 0)$	1 U in $(0, 0, 0)$
1 Ca in $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	1 Ca in $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
2 F in $\pm(u, u, u)$ with $u=0.125$	$2\text{O}_I$ in $\pm(u, u, u)$ with $u=0.109$
2 F in $\pm(v, v, v)$ with $v=0.375$	$2\text{O}_{II}$ in $\pm(v, v, v)$ with $v=0.361$

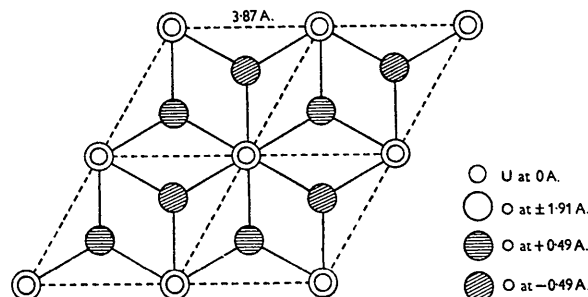


Fig. 2. A layer  $(\text{UO}_2)\text{O}_2$  as found in the  $\text{Ca}(\text{UO}_2)\text{O}_2$  structure. Small circles represent uranium atoms in the plane of the paper. Large circles represent oxygen atoms. The heights in \AA. of the oxygen atoms above or below the plane of the paper are indicated in the figure.

Normal to the threefold axis the  $\text{Ca}(\text{UO}_2)\text{O}_2$  structure contains layers of uranium atoms, the layer separation being 5.84 \AA. The uranyl groups are normal to these layers, and the  $\text{O}_{II}$  atoms are 0.49 \AA. above or below the plane defined by the uranium atoms. Fig. 2 shows the structure of a layer. The structure of calcium uranate can be regarded as a stack of such layers. The calcium atoms are situated half-way between the uranium layers and bind the layers together.

The hexagonal layers  $(\text{UO}_2)\text{O}_2$  shown in Fig. 2 have been found in a great many hexavalent uranium compounds, such as  $\text{UO}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{Li}_2(\text{UO}_2)\text{O}_2$ ,  $\text{Na}_2(\text{UO}_2)\text{O}_2$ ,  $\text{K}_2(\text{UO}_2)\text{O}_2$ . These crystals are either truly hexagonal ( $\text{UO}_3$ ) or orthorhombic pseudo-hexagonal, and all exhibit excellent cleavage parallel to the layers.

If the  $\text{O}_{II}$  oxygen atoms are replaced by fluorine atoms, the composition of the layer shown in Fig. 2 becomes  $\text{UO}_2\text{F}_2$ . Indeed, as shown in an earlier article (Zachariasen, 1948), the structure of uranyl fluoride is built up of such layers.

During the war the writer also investigated the analogous barium compound,  $\text{Ba}(\text{UO}_2)\text{O}_2$  (Zachariasen,

1945). The structure of this compound, which is not isostructural with the corresponding calcium and strontium compounds, was discussed in a recent paper

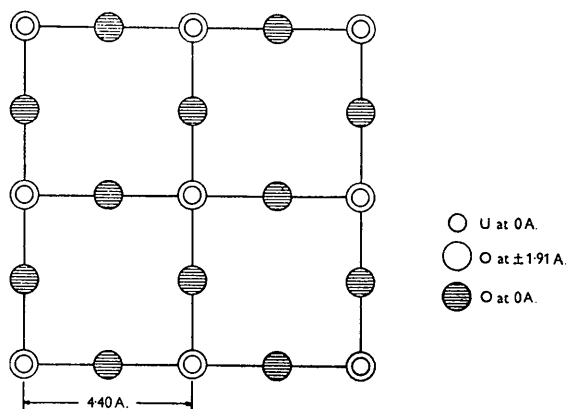


Fig. 3. The tetragonal  $(\text{UO}_2)_2\text{O}_2$  layer which occurs in the structure of  $\text{Ba}(\text{UO}_2)_2\text{O}_2$  proposed by Samson and Sillén.

by Samson & Sillén (1947). These investigators determined the positions of the barium and uranium atoms by means of intensity considerations, and made reasonable guesses as to the location of the oxygen atoms.

The structure proposed for  $\text{Ba}(\text{UO}_2)_2\text{O}_2$  by Samson & Sillén consists of  $(\text{UO}_2)_2\text{O}_2$  layers held by barium atoms situated halfway between the uranium layers. The  $(\text{UO}_2)_2\text{O}_2$  layer in the suggested barium uranate structure is, however, quite different from the one encountered in other uranates. Whereas each uranium atom in  $\text{Ca}(\text{UO}_2)_2\text{O}_2$ ,  $\text{UO}_3$ ,  $\text{UO}_2\text{F}_2$  and in the alkali uranates forms two uranyl bonds and six secondary bonds to other oxygen or fluorine atoms, there are only four of these secondary bonds in barium uranate. The  $(\text{UO}_2)_2\text{O}_2$  layer of barium uranate is shown idealized in Fig. 3.

The writer is indebted to Miss Anne Plettinger who took the X-ray diffraction patterns.

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## Crystal Chemical Studies of the 5f-Series of Elements. V. The Crystal Structure of Uranium Hexachloride

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(Received 20 August 1948)

$\text{UCl}_6$  is hexagonal with three molecules per unit cell. The unit-cell dimensions and the calculated density are:

$$a_1 = 10.95 \pm 0.02 \text{ kX.}, \quad a_2 = 6.03 \pm 0.01 \text{ kX.}, \quad \rho = 3.56 \text{ g.cm.}^{-3}.$$

The space group is  $C\bar{3}m-D_{3d}^3$  and the atomic positions are: 1 U in  $(0, 0, 0)$ , 2 U in  $\pm(\frac{1}{3}, \frac{2}{3}, z)$  with  $z = \frac{1}{2}$ , and three sets of six chlorine atoms in  $\pm(x, 2x, z)$   $(2\bar{x}, \bar{x}, z)$   $(x, \bar{x}, z)$  with parameters as follows:

	$x$	$z$
$\text{Cl}_I$	0.10	0.25
$\text{Cl}_{II}$	0.43	0.25
$\text{Cl}_{III}$	0.77	0.25

The structure is of molecular type. The  $\text{UCl}_6$  molecules are octahedral with  $\text{U-Cl} = 2.42 \pm 0.10 \text{ \AA}$ .

#### Introduction

Uranium forms chlorides  $\text{UCl}_3$ ,  $\text{UCl}_4$ ,  $\text{UCl}_5$  and  $\text{UCl}_6$ . The crystal structures of  $\text{UCl}_3$  (Zachariasen, 1948a) and of  $\text{UCl}_4$  have recently been described. The writer has investigated the structure of  $\text{UCl}_5$  which is monoclinic with four molecules per unit cell. The chlorine positions in the  $\text{UCl}_5$  structure are, however, yet unknown. The present paper discusses the crystal-structure determination of the hexachloride.

A remarkable microsample of uranium chlorides prepared by Dr Sherman Fried was used in the investigation. Within one of the thin-walled glass capillaries used as sample containers for X-ray diffraction specimens on the micro-scale Dr Fried prepared  $\text{UCl}_4$ ,  $\text{UCl}_5$  and  $\text{UCl}_6$ . The three compounds were in three well-separated sublimed zones, green, reddish brown and black in color. Each zone contained only a few micrograms of sublimed material. The black  $\text{UCl}_6$ , being the