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The Crystal Structure of some Alkaline Earth Metal Uranates of the Type M_3UO_6*

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(*Received* 17 *May* 1965 *and in revised form* 30 *July* 1965)

The compounds Ca_3UO_6 and Sr_3UO_6 are isomorphous and can be regarded as deformed substituted perovskite structures. They have been refined by a full-matrix least-squares method using X-ray and neutron-diffraction powder data. The uranium atoms are surrounded by six oxygen atoms at an average distance of 2·13 Å.

Introduction

As part of a programme of research on uranium compounds, a powder diffraction study was undertaken on the alkaline earth metal uranates Ca_3UO_6, Sr_3UO_6 and Ba_3UO_6. The crystal symmetry of the first two compounds had been previously determined to be orthorhombic (Bereznikova, Ippolitova, Simanov & Kovba, 1961; Ippolitova, Bereznikova, Kosynkin, Simanov & Kovba, 1961; Sleight & Ward, 1962) while the symmetry of the latter had been described as cubic by Sleight & Ward (1962).

The calcium and strontium uranates were prepared by igniting stoichiometric mixtures of U_3O_8 and $CaCO_3$ or $Sr(NO_3)_2$ in air at temperatures of 1000°C for periods of weeks (Cordfunke & Loopstra, 1965). The barium uranate had to be prepared by ignition of a stoichiometric mixture of U_3O_8 and $Ba(NO_3)_2$, in a nickel boat in an argon atmosphere at 1000°C, to avoid the reaction of any of the components of the mixture with the normally used platinum container.

The calcium and strontium uranate samples were free from detectable amounts of impurities, but the barium compound showed some very faint impurity lines on its X-ray powder diffraction diagram.

Experimental

X-ray diffractograms of the calcium and strontium uranates were recorded with Ni-filtered Cu $K\alpha$ radiation, on a Philips PW-1050 powder diffractometer, which obviates the need for absorption corrections due to the special sample orientation. In addition, and in order to obtain the highest possible resolution on these powder diagrams, Guinier films of all three samples were taken with Cu $K\alpha$ radiation. These diagrams were superimposed with NaCl lines for calibration purposes.

Neutron-diffraction data of Ca_3UO_6 and Sr_3UO_6 were recorded on the powder diffractometer at the Petten HFR. No absorption corrections were necessary, because of the small absorption of these materials for thermal neutrons. The sample was contained in a cylindrical vanadium sample holder of 0·25 mm wall thickness and 20 mm diameter. Monochromatic radiation with a wavelength of 1·094 Å was obtained from the 200 reflexion of a copper monochromating crystal. Soller slits of 5′ angular divergence were mounted in front of the BF_3 counter and slits of $5\frac{1}{2}'$ angular divergence were placed between the reactor and the monochromator. With the reactor operating at 20 MW thermal power, it took one week to collect a set of data.

Unit-cell determination

An inspection of the Guinier films showed, in all cases, line splitting that indicated a lower symmetry than was previously determined. The special focusing action of this type of camera, which reduces the α_1 and α_2 resolution, made it possible to observe these line splittings with an accuracy of 0·025° in 2θ. In the case of the calcium and strontium compounds, it was possible to account for this by taking a monoclinic cell instead of an orthorhombic cell. The barium uranate lines

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* Work sponsored jointly by Reactor Centrum Nederland, The Netherlands, and Institutt for Atomenergi, Norway.

could be indexed, except for three very weak lines, on a tetragonal cell which was one-half of the previously mentioned cubic cell. The cell constants were adjusted by means of a least-squares technique to give the best agreement between calculated and observed line spacings, expressed as Q values where $Q=1/d^2\times10^4$ Å^{-2}. A list of these values appears in Table 1, and the cell constants are shown in Table 2.

It may be noticed here, that on these Guinier films, only reflexions with $h+k+l=2n$, indicating a body-centred cell, were recorded. This is partly caused by the relatively short exposure-times, but also by the fact that the uranium and alkaline earth metal ions, which act as heavy scatterers for X-rays, form an approximately body-centred unit-cell. Longer exposures on the X-ray spectrometer yield lines which are no longer consistent with this condition. In particular, reflexions obtained by neutron diffraction, in which case all atoms have approximately the same scattering power, show clearly that the actual cell is not body-centred (Table 5).

Structure determination

In view of the fact that there was some uncertainty in the choice of the unit cell of Ba_3UO_6 owing to the presence of three unindexed lines, it was decided not to pursue the analysis of this compound any further.

An inspection of the X-ray and neutron diffraction diagrams of Ca_3UO_6 showed that all $0k0$ reflexions with k odd were systematically absent, a condition which corresponds to that of the monoclinic space-groups $P2_1$ or $P2_1/m$. Using the corrected peak intensities of 43 well resolved lines on the Guinier film of this uranate, a three-dimensional Patterson synthesis

Table 1. *Observed and calculated Q values*

$Q=10^4\times1/d^2$ Å^{-2}

Ca_3UO_6			Sr_3UO_6			Ba_3UO_6		
hkl	Q_{calc}	Q_{obs}	*hkl*	Q_{calc}	Q_{obs}	*hkl*	Q_{calc}	Q_{obs}
011	427	426	011	399	396	011	378	376
$10\bar{1}$	446	447	$10\bar{1}$	417	416	002	500	503
101	454	455	101	420		110	506	
002	581	582	110	544	544	020	1013	1010
110	587	586	002	547		121	1391	1389
020	1127	1127	020	1044	1048	004	2001	1998
$11\bar{2}$	1159	1159	$11\bar{2}$	1088	1089	220	2025	2024
112	1176	1176	112	1093		031	2403	2403
200	1219	1218	200	1127	1129	132	3032	3033
$12\bar{1}$	1573	1573	$12\bar{1}$	1465	1457	231	3416	3412
121	1581	1581	121	1467		040	4050	4046
013	1588	1588	013	1492	1495	141	4428	4423
103	1624	1626	$21\bar{1}$	1522	1525	006	4502	4495
$21\bar{1}$	1638	1637	211	1528		330	4556	4552
022	1707	1709	022	1594	1590	240	5063	5056
$20\bar{2}$	1783	1783	$20\bar{2}$	1668	1662	143	5429	5425
202	1817	1817	202	1672	1679	341	6453	6459
004	2322	2323	220	2174	2175			
220	2346	2346	004	2187	2185			
031	2680	2680	031	2494	2489			
$12\bar{3}$	2782	2781	$12\bar{3}$	2555	2548			
$21\bar{3}$	2781	2782	$21\bar{3}$	2611	2614			
$22\bar{2}$	2910	2909	213	2626	2628			
114	2926	2924	$13\bar{2}$	3183	3186			
222	2943	2942	132	3188				
310	3025	3025	024	3234	3244			
$13\bar{2}$	3412	3412	$20\bar{4}$	3303	3301			
132	3429	3429	$31\bar{2}$	3335	3342			
024	3449	3448	312	3351	3358			
$20\bar{4}$	3508	3507	015	3679	3677			
$31\bar{2}$	3581	3579	$32\bar{1}$	3715	3720			
015	3910	3909	321	3723	3728			
321	4028	4028	040	4190	4194			
040	4507	4506	041	4327	4326			
$22\bar{4}$	4635	4634	224	4372	4372			
224	4702	4704	400	4506	4499			
400	4877	4877						
$32\bar{3}$	5139	5142						

Unindexed and probably impurity lines:
2070, 3080 and 6051

Table 2. *Unit-cell dimensions*

Uranate	*a* (Å)	*b* (Å)	*c* (Å)	*α*	*β*	*γ*
Ca	5·7278 ± 0·0005	5·9583 ± 0·0005	8·3008 ± 0·0007	90	90·573 ± 0·008	90
Sr	5·959 ± 0·002	6·179 ± 0·002	8·553 ± 0·004	90	90·19 ± 0·04	90
Ba	6·285 ± 0·002	6·285 ± 0·002	8·943 ± 0·006	90	90	90

was computed which yielded approximate positions for the U and three Ca atoms.

The U–Ca peaks were markedly elongated in the *y* direction, indicating that they were lying slightly out of the *XZ*-plane. This eliminates the possibility that this plane can be a mirror plane, and this, therefore, leaves only $P2_1$ as a possible choice. In addition, because the U atom was not in a special position, and only one U–U vector was found in the Patterson synthesis, it was concluded that there were only two molecules of Ca_3UO_6 in the unit cell. This was later confirmed by density measurements.

A three-dimensional electron-density synthesis with phases given by U and the three Ca atoms in the asymmetric unit cell yielded improved coordinates for these atoms and also six rather badly defined peaks. A repeated application of this procedure improved the shape of these peaks, and subsequently they were identified as belonging to the six oxygen atoms in the asymmetric unit cell. The fact that positions of oxygen atoms could be obtained from these rather inaccurate X-ray diffraction data was surprising and may be regarded as purely fortuitous: the same treatment of strontium uranate failed to reveal the positions of the oxygen atoms.

In view of the close resemblance between the calcium- and strontium-uranate X-ray and neutron-diffraction diagrams, these compounds can be regarded as isomorphous, and no further determination of the strontium-uranate structure was required at this stage. The X-ray diffraction diagram of the barium compound also shows a resemblance to those of the other two uranates, but without a neutron diffraction diagram it can only be assumed that the cell formed by the heavy atoms will be isomorphous with the others.

Structure refinement

While the Guinier-film intensities were well resolved, their peak intensities, which were not corrected for absorption, could only be regarded as rather crude approximations to the integrated intensities that actually should be used for further refinement of the structure. However, the integrated intensities available from the X-ray and neutron diffraction diagrams suffered from overlap to such an extent that it was not possible to separate the peaks with any degree of accuracy. Resort, therefore, had to be taken to a special procedure that made full use of the information contained in these accurately measured, but overlapping, intensities. To this end, a structure-factor least-squares program was written that was especially adapted to the particular conditions met in powder-diffraction work.

The program is coded in machine language and uses the full-matrix refinement method. This requires a large storage capacity of the computer: with the available Electrologica X-1 computer, having a storage capacity of 8192 words, it is possible to refine up to 33 selected parameters simultaneously. These parameters consist of the overall isotropic temperature factor, the overall scale factor, and anyone of the individual isotropic temperature factors or atomic coordinates. The function to be minimized is defined as $\sum\limits_i w\,(\sum\limits_r jF^2_{\rm obs} - \sum\limits_r jF^2_{\rm calc})^2$ where $F_{\rm obs}$ and $F_{\rm calc}$ are the observed and calculated structure factors, j is the multiplicity of the reflexion, w its weight, $\sum\limits_r$ the sum of the overlapping reflexions which are measured as one intensity, and $\sum\limits_i$ the sum over the measured intensities, *i.e.* $\sum\limits_r jF^2_{\rm obs}$ after correcting for Lorentz (and polarization) factors. The only restriction on the structures to be refined is that their symmetry should be lower than tetragonal (*i.e.* no permutations in the coordinates of the equivalent positions are allowed). In spite of the use of a full-matrix refinement procedure, it takes up to ten cycles to refine a structure. In addition, it is necessary to apply a 'relaxation factor' to the calculated parameter shifts. This factor sometimes has to be as small as 0·2, particularly when the excess of the number of intensities over the number of least-squares parameters is not very large or when the initial parameters have been badly chosen.

The X-ray scattering factors for the U^{6+}, Ca^{2+} and Sr^{2+} ions and the *O* atoms, used in the refinement of these uranate structures, were those computed by Cromer & Waber (1964). The neutron scattering-lengths were taken to be 8·5 for U, 4·9 for Ca, 5·7 for Sr, and 5·77 for *O* (all in units of 10^{-13} cm). No attempt was made to refine the individual isotropic temperature factors, because these appeared to be ill defined because of the small range (0·11 Å^{-2}) of $\sin^2\theta/\lambda^2$ over which the intensities were measured. Instead, these temperature factors were set at initial values and corrected with the calculated change in the overall isotropic temperature factor. The values were $B = 0{\cdot}1$ Å^2 for the U atom, 0·6 Å^2 for Ca, 0·3 Å^2 for Sr and 1·5 Å^2 for the *O* atom.

For the refinement of calcium uranate, 45 integrated intensities, comprising 100 independent reflexions, were measured from the X-ray diffractogram, and, in addition, 17 unobserved reflexions were included having intensities arbitrarily set at one-tenth of the integrated background at their calculated position. All were corrected for Lorentz and polarization factors. In the absence in this case of any reliable criterion for assessing the accuracy of the measured intensities, the least-squares weights were put equal to one for the observed and to one-tenth for the unobserved reflexions. With the coordinates from the final electron-density synthesis as initial parameters, twelve refinement cycles were needed to reduce the *R* index, defined as

$$\sum_i \left| \sum_r jF^2_{\rm obs} - \sum_r jF^2_{\rm calc} \right| / \sum_i \sum_r jF^2_{\rm obs},$$

from 0·208 to 0·051. At this stage no further reduction in the value of the minimum function could be obtained, and all calculated shifts were less than $0{\cdot}3\sigma$

where σ is the standard deviation in the parameter computed in the usual manner from the least-squares calculation.

The neutron-diffraction counter data of Ca_3UO_6 consisted of 33 intensities and 17 unobserv edintensities which were put equal to half the standard deviation of the background at their calculated positions. These intensities, after having been corrected for the Lorentz factor, were used to refine the coordinates obtained from the least-squares refinement of the X-ray data. The weight of the reflexions was calculated from the expression $w=1/(N_p+N_b)$ where N_p is the integrated peak plus background intensity and N_b the background intensity. The weights of the unobserved reflexions were arbitrarily set at one tenth of this value. It took eight cycles to reduce R from 0·19 to 0·061. The final coordinates, together with those obtained from the X-ray refinement, are listed in Table 3.

The refinement of strontium uranate was carried out with neutron diffraction data only. There were available 38 intensities and 19 unobserved intensities which were treated in the same way as described above. With

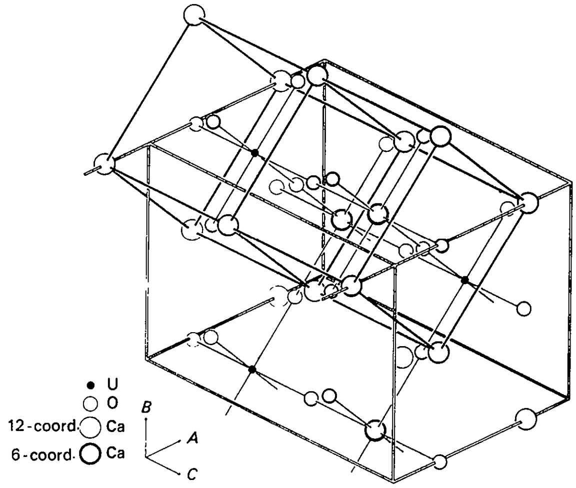

Fig. 1. Perspective drawing of the idealized structure of Ca_3UO_6. The double lines indicate the actual unit cell of the uranate and the heavy lines the perovskite-type subcell.

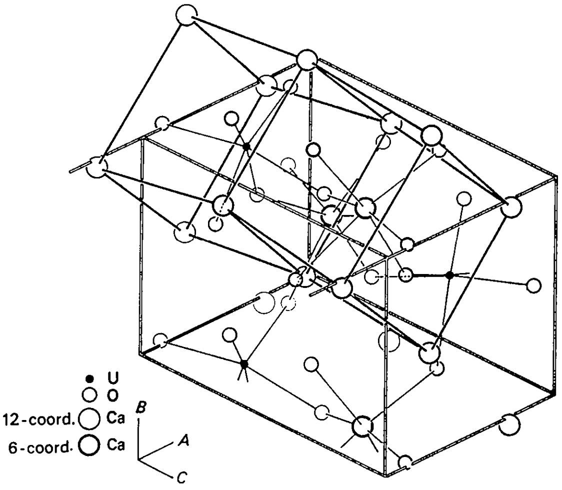

Fig. 2. Perspective drawing of the actual structure of Ca_3UO_6, showing clearly the deformation of the idealized structure of Fig. 1.

Table 3. *Final least squares coordinates of* Ca_3UO_6

	X-ray diffraction						Neutron diffraction					
	x/a	*σ(x/a)*	*y/b*	*σ(y/b)*	*z/c*	*σ(z/c)*	*x/a*	*σ(x/a)*	*y/b*	*σ(y/b)*	*z/c*	*σ(z/c)*
U	0·2538	0·0008	0·0000	—	0·2516	0·0004	0·2568	0·0066	0·0000	—	0·2441	0·0041
Ca(1)	0·2428	0·0059	0·9961	0·0180	0·7448	0·0019	0·2571	0·0121	0·9893	0·0102	0·7398	0·0064
Ca(2)	0·2652	0·0051	0·4612	0·0089	0·9975	0·0022	0·2708	0·0084	0·4467	0·0071	0·0151	0·0053
Ca(3)	0·7628	0·0041	0·0498	0·0082	0·4932	0·0024	0·7618	0·0078	0·0595	0·0075	0·4685	0·0046
O(1)	0·6481	0·0075	0·4235	0·0137	0·5142	0·0052	0·6504	0·0042	0·3894	0·0080	0·4959	0·0054
O(2)	0·5912	0·0086	0·1577	0·0126	0·2140	0·0050	0·5695	0·0089	0·1394	0·0065	0·2138	0·0048
O(3)	0·0491	0·0070	0·2697	0·0114	0·3300	0·0109	0·0655	0·0073	0·2429	0·0087	0·3261	0·0042
O(4)	0·1208	0·0087	0·0824	0·0166	0·0089	0·0059	0·1083	0·0071	0·0290	0·0063	0·0116	0·0051
O(5)	0·0307	0·0093	0·3209	0·0144	0·6568	0·0103	0·0386	0·0063	0·2986	0·0056	0·6711	0·0040
O(6)	0·5927	0·0100	0·1827	0·0140	0·7911	0·0083	0·5762	0·0084	0·1764	0·0078	0·8168	0·0050

Table 4. *Final least-squares coordinates of* Sr_3UO_6

	x/a	*σ(x/a)*	*y/b*	*σ(y/b)*	*z/c*	*σ(z/c)*
U	0·2503	0·0045	0·0000	—	0·2424	0·0023
Sr(1)	0·2420	0·0041	0·9917	0·0064	0·7564	0·0026
Sr(2)	0·2505	0·0042	0·4641	0·0060	0·0010	0·0037
Sr(3)	0·7572	0·0051	0·0588	0·0053	0·5081	0·0038
O(1)	0·6594	0·0041	0·4012	0·0050	0·4946	0·0036
O(2)	0·5328	0·0043	0·1287	0·0053	0·2324	0·0036
O(3)	0·1014	0·0037	0·2466	0·0053	0·3075	0·0022
O(4)	0·1312	0·0067	0·0003	0·0048	0·0098	0·0037
O(5)	0·0750	0·0041	0·2947	0·0066	0·6753	0·0032
O(6)	0·5335	0·0032	0·1910	0·0038	0·8152	0·0017

the calcium uranate coordinates as initial parameters, 9 cycles were needed to decrease R from 0·22 to 0·094. A list of the final coordinates appears in Table 4.

The values of jF^2_{obs} and jF^2_{calc} for the neutron diffraction data of the calcium and strontium compounds and of the X-ray data of the calcium compound are listed in Table 5.

Discussion

The two sets of coordinates for calcium uranate (see Table 3) can be considered to be equal within the limits set by their standard deviations. For a bond length and bond angle calculation however, it was decided to use the X-ray coordinates of the U and Ca atoms

Table 5. *Calculated and observed structure factors of* Ca_3UO_6 *and* Sr_3UO_6

Neutron data in units of $0{\cdot}25 \times 10^{-26}$ cm² and X-ray data in units of 10^2e^2

Ca_3UO_6				
hkl	X-ray		neutron	
	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$
001	< 1	3	< 3	4
100	< 1	0	< 6	4
011	796	825		
10$\bar{1}$				
101	692	735	346	293
002				
110	1143	1242	393	454
11$\bar{1}$				
111	46	37	35	139
012	< 1	2	< 16	31
10$\bar{2}$	< 1	2	< 16	110
102	< 1	3	< 16	12
020	868	958		
11$\bar{2}$				
112	3596	3922		
200	839	935	1436	1694
021	< 3	1		
003	< 4	5	262	336
20$\bar{1}$	< 3	2		
201	< 3	1	40	13
120	< 3	9	193	165
210	59	44	1204	1244
12$\bar{1}$				
121				
013				
10$\bar{3}$	1665	1851		
103				
21$\bar{1}$				
211	1784	1796	4621	4404
022	369	430	558	576
20$\bar{2}$	186	231		
202	186	216	239	177
11$\bar{3}$				
113	140	87	1407	1331
12$\bar{2}$				
122	75	63	1643	1676
21$\bar{2}$	< 4	6		
212	< 4	4	253	240
004				
220	3135	3143	4861	5016
023	60	36	206	285
22$\bar{1}$				
221				
20$\bar{3}$	124	84	606	608
203	< 5	0		
014	< 5	1	47	55
10$\bar{4}$	< 5	4		
104	< 5	10		
031	472	513	240	268
12$\bar{3}$				
300				
123				
21$\bar{3}$	1457	1505	980	867
213				
130	1480	1453	1191	1211
30$\bar{1}$				
11$\bar{4}$				
301				
22$\bar{2}$				
114				
222	3173	3100	2822	2793
13$\bar{1}$				
131	301	184		
310	540	574	2175	2219
032	< 8	2	181	168
31$\bar{1}$	< 6	13		
311	53	27	488	492
30$\bar{2}$	< 6	2	< 61	1
302	< 8	2	< 61	28
13$\bar{2}$				
132				
024	4626	4595	5581	5478
20$\bar{4}$	766	772		

Ca_3UO_6				
hkl	X-ray		neutron	
	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$
204				
31$\bar{2}$	2760	2646		
22$\bar{3}$				
005				
312	1750	1676		
223	13	22	9181	8926
12$\bar{4}$	< 9	11		
230	< 9	6		
124	< 10	0	307	385
21$\bar{4}$	< 10	1	70	123
033				
214				
320	404	491		
23$\bar{1}$				
231				
015				
10$\bar{5}$	1783	1806	1870	2136
105	257	276	75	123
32$\bar{1}$				
30$\bar{3}$				
321	1323	1323	644	641
303	195	222	< 75	25
13$\bar{3}$				
133				
11$\bar{5}$	138	111	701	773
115	< 8	21		
31$\bar{3}$	< 11	7		
23$\bar{2}$	< 12	3		
232	32	21		
313	< 9	8		
32$\bar{2}$	< 9	9	3119	3194
322	9	5		
040	510	506	340	421
22$\bar{4}$				
041	1338	1301		
224	1221	1215	2199	2250
025	< 13	4		
20$\bar{5}$	< 13	0		
140	< 15	26		
034	< 21	2	2691	2675
400			292	309
205	551	573	< 88	5
14$\bar{1}$			< 93	110
141	899	950	190	298
40$\bar{1}$	< 16	2		
30$\bar{4}$	< 16	0		
23$\bar{3}$				
12$\bar{5}$				
401				
125				
233				
042				
21$\bar{5}$				
304	3178	3129		
32$\bar{3}$				
13$\bar{4}$				
410				
215				
134				
323				
006	2662	2658		
330				
41$\bar{1}$				
31$\bar{4}$				
411	1616	1776		
14$\bar{2}$				
314				
142				
33$\bar{1}$				
40$\bar{2}$				
331	6830	7252		
402				
10$\bar{6}$				
016	236	241		

Sr_3UO_6		
hkl	neutron	
	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$
001	< 1	3
100	8	1
011	197	156
10$\bar{1}$		
101	100	68
002		
110	289	500
11$\bar{1}$		
111	142	93
012		
10$\bar{2}$		
102	143	73
020		
11$\bar{2}$		
112		
200	2213	2672
021		
003	112	273
20$\bar{1}$	< 13	17
201	< 13	1
120	163	251
210	951	1054
12$\bar{1}$		
121	869	879
013		
10$\bar{3}$		
103		
21$\bar{1}$		
211	3220	3329
022	1024	935
20$\bar{2}$		
202	902	484
11$\bar{3}$		
113	1415	1365
12$\bar{2}$		
122		
21$\bar{2}$		
212	1858	1722
004		
220	6970	7278
023		
22$\bar{1}$		
221	790	725
20$\bar{3}$	< 23	2
203	< 23	15
014	74	124
10$\bar{4}$	< 24	35
104	< 24	40
031	44	35
12$\bar{3}$		
300		
123	693	582
21$\bar{3}$		
213		
130		
30$\bar{1}$		
301	1705	2111
22$\bar{2}$		
11$\bar{4}$		
222		
114	2235	2000
13$\bar{1}$		
131		
310	2518	2421
032		
31$\bar{1}$		
311	781	827
30$\bar{2}$	230	323
302	< 50	80
13$\bar{2}$		
132	3151	3395
024	3538	3571

Sr_3UO_6		
hkl	neutron	
	$\sum_r jF^2_{\text{obs}}$	$\sum_r jF^2_{\text{calc}}$
20$\bar{4}$		
204		
31$\bar{2}$		
312	11091	10250
22$\bar{3}$	82	129
223	< 32	18
005	< 32	7
230		
12$\bar{4}$		
124	292	301
21$\bar{4}$		
320		
214		
033		
23$\bar{1}$		
231	1110	1186
015		
10$\bar{5}$		
105		
32$\bar{1}$		
321		
30$\bar{3}$		
303	1126	1230
13$\bar{3}$		
133	723	716
11$\bar{5}$		
115		
31$\bar{3}$		
23$\bar{2}$		
232		
313	1284	2245
32$\bar{2}$	137	151
322	< 47	66
040	931	921
041		
22$\bar{4}$		
224	5297	5200
025		
140		
400	2679	2683
20$\bar{5}$		
034		
205		
14$\bar{1}$		
141		
40$\bar{1}$		
401	566	755
23$\bar{3}$		
30$\bar{4}$		
233		
042		
304		
12$\bar{5}$		
125		
410		
21$\bar{5}$		
32$\bar{3}$		
13$\bar{4}$		
215		
323		
134	6745	6629
330		
41$\bar{1}$		
411		
006	762	784
31$\bar{4}$		
314		
14$\bar{2}$		
142		
33$\bar{1}$		
331		
40$\bar{2}$		
402	965	1223

and the neutron coordinates of the *O* atoms. This was done because X-ray diffraction techniques can define the position of the heavy U and Ca atoms better than the position of the relatively light *O* atoms, a fact which is brought out by the smaller standard deviations in the coordinates of the former atoms. Table 6 lists the more important atomic distances and angles of the calcium and strontium compounds.

Table 6. *Atomic distances and angles*

	Distances	
	Ca_3UO_6	Sr_3UO_6
U —O(1)	2·26 ± 0·09 Å	2·39 ± 0·12 Å
U —O(2)	2·02 ± 0·10	1·86 ± 0·12
U —O(3)	1·91 ± 0·09	1·85 ± 0·09
U —O(4)	2·16 ± 0·08	2·11 ± 0·12
U —O(5)	2·16 ± 0·07	2·42 ± 0·12
U —O(6)	2·24 ± 0·09	2·36 ± 0·09
M(1)–O(1)	2·19 ± 0·11	2·30 ± 0·12
M(1)–O(2)	2·41 ± 0·21	2·62 ± 0·15
M(1)–O(3)	2·39 ± 0·17	2·60 ± 0·11
M(1)–O(4)	2·36 ± 0·09	2·27 ± 0·13
M(1)–O(5)	2·23 ± 0·19	2·23 ± 0·16
M(1)–O(6)	2·27 ± 0·15	2·19 ± 0·12

	Angles	
	Ca_3UO_6	Sr_3UO_6
U–O(1)–M(1)	134·0 ± 2·8°	139·5 ± 3·4°
U–O(2)–M(1)	137·9 ± 2·7	146·0 ± 3·8
U–O(3)–M(1)	146·4 ± 2·3	142·6 ± 3·0
U–O(4)–M(1)	137·1 ± 2·4	144·3 ± 5·0
U–O(5)–M(1)	140·6 ± 2·0	134·6 ± 3·4
U–O(6)–M(1)	135·2 ± 3·1	147·5 ± 2·4

Fig. 1 shows a perspective drawing of an idealized substituted perovskite structure. The large parallellepiped indicates the unit cell on which the uranate structures have been described. The two smaller cubes are octants of the cubic unit cell on which the perovskite structure is normally described. The cube corners are occupied by alkaline earth metal ions which are coordinated by twelve oxygen atoms. Their centres are alternately occupied by a uranium ion and an alkaline earth metal ion, each surrounded by an octahedral configuration of six O atoms. The position of these O atoms is slightly off the centre of the cube faces in the direction of the uranium ion. This idealized structure is supposed to be purely ionic and this results in the U–O–Ca bonds being exactly collinear.

It is clear from Fig. 2, which is a perspective drawing of the actual Ca_3UO_6 structure, that the essential features of the idealized structure have been retained. The structure is however, markedly deformed. In particular the U–O–Ca bonds are no longer collinear, but make an average angle of approximately 140°. This is caused by the covalent character of these bonds which, by using the non-collinear 2*p* orbitals of the O atom, are prevented from being at an angle of 180° to each other.

From an inspection of Table 6, it is clear that the six U–O coordinate bonds are not equal. However, some significance can be attached to their average value if the root mean square (r.m.s.) deviation of this value does not appreciably exceed the average standard deviation ($\bar{\sigma}$) of the individual bonds. A list of the appropriate values, together with those of the Ca–O and Sr–O coordinate bonds, appears in Table 7. The r.m.s. deviation of the average U–O bond in Sr_3UO_6 is seen to exceed more than twice the average standard deviation which indicates that no significance can be attached to this value. The other three bond lengths, however, constitute good averages, on the ground of the agreement between their r.m.s. deviation and their average standard deviation.

Table 7. *Average values, root mean square deviations* (r.m.s.) *and average standard deviations* ($\bar{\sigma}$) *of some bonds*

	Distance	$\bar{\sigma}$	r.m.s.
U(Ca)–O	2·12 Å	0·09 Å	0·12 Å
U(Sr) –O	2·16	0·11	0·21
Ca(1) –O	2·31	0·15	0·08
Sr(1)—O	2·37	0·13	0·17

Assuming an O^{2-} – radius of 1·4 Å, the following ionic radii are obtained: 0·74 Å for U^{6+}, 0·91 Å for Ca^{2+} and 0·97 Å for Sr^{2+}. The latter two radii are shorter than the values normally stated, *i.e.* 0·99 and 1·12 Å for Ca^{2+} and Sr^{2+} respectively (Evans, 1964). This also points to the covalent character of the coordinate bonds. However, in view of their large standard deviations no further significance can be attached to these values.

The author wishes to thank Dr E. H. P. Cordfunke for supplying the uranate samples and Dr B. O. Loopstra for much helpful criticism.

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