Literatur

BAKER, C. L. & JUE, L. R. (1938). *J. Phys. Chem.* **42**, 165.

BAKER, C. L., JUE, L. R. & WILLS, J. H. (1950). *J. Amer. Chem. Soc.* **72**, 5374.

BAKER, C. L., WOODWARD, T. & PABST, A. (1933). *Amer. Min.* **18**, 206.

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.

HOWELLS, E. R., PHILLIPS, D. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

LANGE, H. & STACKELBERG, M. VON (1948). *Z. anorg. Chem.* **256**, 273.

MEGAW, H. D. (1952). *Acta Cryst.* **5**, 477.

SMITH, J. V. & BAILEY, S. W. (1963). *Acta Cryst.* **16**, 801.

THILO, E. & MIEDREICH, W. (1951). *Z. anorg. Chem.* **267**, 76.

THILO, E., WIEKER, W. & STADE, H. (1965). *Z. anorg. Chem.* **340**, 261.

Acta Cryst. (1966). **21**, 589

The Structure of β-UO$_3$*

BY P. C. DEBETS

Reactor Centrum Nederland, Petten, The Netherlands

(*Received* 28 *January* 1966)

The structure of β-UO$_3$ has been determined by means of X-ray and neutron-diffraction powder data. Ten formula units are contained in the monoclinic unit cell, which belongs to the space group $P2_1$. The structure can be regarded as consisting of layers, perpendicular to the monoclinic axis, interconnected by uranyl groups.

Introduction

Uranium trioxide has at least five different polymorphs ($\alpha-\varepsilon$) for which a phase diagram has been suggested recently (Cordfunke & Aling, 1965). Reliable structural data are available only for γ-UO$_3$ (Engmann & de Wolff, 1963). As a contribution to the knowledge of this system this paper presents the structure determination of β-UO$_3$, based on X-ray and neutron powder diffraction data.

Experimental

Polycrystalline samples of β-UO$_3$ were prepared in two ways:

(*a*) By calcining 'ADU' (the reaction product of uranyl nitrate with ammonia) in air at 450–500°C.

(*b*) By calcining uranyl nitrate in air at the same temperatures. In this case rapid heating to the desired temperature is essential because otherwise γ-UO$_3$ will be formed.

The products were heated at 500°C until no further growth of the crystallites was observed, generally 4 to 6 weeks. During this period the temperature was not allowed to exceed 500°C to minimize recrystallization to γ-UO$_3$, the stable modification (Cordfunke & Aling, 1965). From both starting materials a pure and stoichiometric β-UO$_3$ could be obtained, but the use of uranyl nitrate resulted in most cases in a sample of better crystallinity.

The ultimate crystallite size along the *b* axis was measured from the width of the 040 reflexion to be about 600 Å, neglecting disorder and deformation effects. The sizes along the other axes could not be measured, because no other suitable reflexion, free from overlap, was available. Three different samples with maximum crystallinity were used to measure peak positions and intensities in the X-ray diffraction pattern. The neutron diffraction data were collected on only one sample.

The X-ray diffraction diagrams were obtained by means of a Philips diffractometer equipped with a proportional counter with pulse-height-discrimination, using Cu $K\alpha$ radiation. The intensities were counted manually with intervals of 0·02 to 0·1° in 2θ, depending on the slope of the curve. After plotting, the areas of the peaks were measured with a planimeter. 80 Intensities could be measured up to $\sin\theta/\lambda=0{\cdot}3340$ Å^{-1}, consisting of 171 reflexions. In addition, 23 reflexions which were not observed were included with intensities arbitrarily set at half of the lowest observed intensity.

The neutron diffraction data were recorded on the powder diffractometer at the Petten High Flux Reactor. The sample was contained in a cylindrical vanadium sample holder of 0·2 mm wall thickness and 20 mm diameter. Monochromatic radiation with a wavelength of 1·096 Å was obtained from the second order reflexion of a copper (100) plane. Soller slits of 5½′ and 5′ angular divergence were mounted between

---

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

the reactor and the monochromator and in front of the BF_3 detector respectively. Eighty-four intensities were measured up to $\sin\theta/\lambda = 0{\cdot}3750$ Å^{-1}, containing 233 reflexions, to which number 4 reflexions which were not observed were added.

Structure determination

β-UO_3 has monoclinic symmetry. The unit-cell dimensions, as determined by least squares from the X-ray powder pattern, are: $a = 10{\cdot}34 \pm 0{\cdot}01$; $b = 14{\cdot}33 \pm 0{\cdot}01$; $c = 3{\cdot}910 \pm 0{\cdot}004$ Å; $\beta = 99{\cdot}03 \pm 0{\cdot}02°$.

From the systematic absence of $0k0$ reflexions with k odd it follows that the space group is $P2_1/m$ or $P2_1$ (Debets, 1964). The unit cell contains 10 formula units.

From the X-ray pattern a pseudo-hexagonal subcell could be found with edges $a \simeq 3{\cdot}9$ Å and $c = 7{\cdot}16$ Å, the volume of which (95·3 Å^3) is one-sixth of that of the total cell. The subcell reflexions are those with k even and $h + 2l = 3n$. The ratio between the magnitudes of the structure factors of these reflexions is roughly 5:3:1, as given in Table 1. These conditions can be satisfied only if the uranium atoms occupy the positions given in Table 2.

Table 1. *Relative magnitudes of subcell structure factors*

h	k	l	F
even	$4n$	even	5
even	$4n+2$	even	1
even	$4n$	odd	1
even	$4n+2$	odd	5
odd	$2n$		3

Table 2. *Approximate positions of uranium atoms*

In space group $P2_1$ (origin on 2_1)				In space group $P2_1/m$ (origin at centre of symmetry)			
	x/a	y/b	z/c		x/a	y/b	z/c
2(*a*)	0·00	0·00	0·00	2(*a*)	0·00	0·00	0·00
2(*a*)	0·33	0·00	0·67	4(*f*)	0·33	0·00	0·67
2(*a*)	0·67	0·00	0·33	2(*e*)	0·17	0·25	0·83
2(*a*)	0·17	0·25	0·83	2(*e*)	0·67	0·25	0·83
2(*a*)	0·67	0·25	0·83				

As in the space group $P2_1/m$ the X-ray intensities of several non-subcell reflexions could not be accounted for, $P2_1$ was selected. The uranium positions were refined by three-dimensional differential electron-density syntheses, using the X-ray scattering factors of Cromer & Waber (1964). With the resulting parameters a difference synthesis was calculated from the neutron diffraction data, using the scattering lengths $0{\cdot}85 \times 10^{-12}$ cm and $0{\cdot}577 \times 10^{-12}$ cm for uranium and oxygen respectively. From a series of successive difference syntheses twelve out of the total of fifteen oxygen atoms could be placed. Geometrical considerations then led to tentative positions for the three remaining oxygen atoms, *viz.* O(3), O(6) and O(9) (see Table 4).

Structure refinement

The oxygen positions were refined by a least-squares analysis of the neutron diffraction data on an Electrologica X-1 computer. Because of the poor crystallinity of the samples and the large number of reflexions the diffraction diagram suffered severely from overlap. The least-squares program minimizes the quantity $\sum_i w(\sum_r j_{hkl}F^2_{\text{obs}} - \sum_r j_{hkl}F^2_{\text{calc}})^2$ by a full-matrix refinement technique (Rietveld, 1966). Here $\sum_i$ is the sum over all peaks which can be separated in the diagram, w is the weight of one peak, $\sum_r$ is the sum over the overlapping reflexions in such a peak and j_{hkl} the multiplicity factor of a reflexion. The weights used were inversely proportional to the variances of the measured intensities, $w = k/\sigma^2$, the largest weight being taken as unity. For isolated peaks $\sigma^2 = \sigma_P^2 + \sigma_B^2$, where σ_P is the standard deviation of peak and σ_B that of the background. As σ is the square root of the number of registered counts this can be written as $\sigma^2 = N_P + N_B$, N_P and N_B being the intensities of peak and background respectively. For overlapping peaks the inaccuracies in the measurements of both peak area and background were in many cases much higher than the standard deviations calculated in this way. In such cases the estimated inaccuracies were used instead of σ.

The program allows up to 33 parameters to be refined in one cycle. As a result the positional parameters of only ten atoms could be refined simultaneously. No attempt was made to refine the individual isotropic temperature factors, because these appeared to be ill defined owing to the small range of $\sin\theta/\lambda$ over which the intensities could be measured. Instead, the temperature factors for oxygen and uranium were estimated from the difference syntheses and corrected by multiplying by the calculated change in the overall isotropic temperature factor. The final values were 1·1 Å^2 for the uranium atoms and 1·6 Å^2 for the oxygen atoms.

After twenty-seven cycles the resulting parameters were entered in a least-squares refinement of the X-ray data. For the oxygen parameters these calculations resulted in extremely large standard deviations. Therefore the X-ray data were used for the refinement of the uranium parameters only, inserting the oxygen parameters at fixed values. After five cycles the R index, defined as $\sum_i |\sum_r j_{hkl}F^2_{\text{obs}} - \sum_r j_{hkl}F^2_{\text{calc}}| / \sum_i \sum_r j_{hkl}F^2_{\text{obs}}$ was reduced to 8·1%. At this stage no further reduction of the minimum function could be obtained. With these parameters ten more least-squares cycles were performed on the neutron data, keeping the uranium positions constant. This resulted in a final R value for the neutron data of 7·4%. From another least-squares refinement cycle with the X-ray data it was found that the uranium parameters were not influenced by the shifts obtained for the oxygen atoms.

The calculated and observed structure factors for both the X-ray and the neutron pattern are listed in Table 3, the final coordinates in Table 4.

Discussion

As can be seen from Table 4 and Figs. 1 and 2 three uranium atoms, *viz.* U(1), U(2) and U(3), are found in or very near to the plane $y=0$, in which they form an almost perfect hexagonal pattern, repeated at $y=\frac{1}{2}$ because of the screw axis. In these planes they are connected by the oxygen atoms O(1), O(2), O(3), O(4) and O(5). In this way layers are formed at distances of 7·16 Å. Halfway between these layers the uranium atoms U(4) and U(5) and the oxygen atoms O(12), O(13), O(14) and O(15) are situated (see Fig. 3). These oxygen atoms are bonded to only one uranium atom. U(4) and U(5) are connected to the layers at $y=0$ and

Table 4. *Final parameters*

	x/a	y/b	z/c	σ_x	σ_y	σ_z
U(1)	0·989	0	0	0·004	—	0·014
U(2)	0·327	0·970	0·671	0·004	0·002	0·012
U(3)	0·667	0·997	0·332	0·004	0·003	0·013
U(4)	0·169	0·229	0·806	0·003	0·003	0·008
U(5)	0·676	0·256	0·864	0·003	0·002	0·007
O(1)	0·061	0·968	0·511	0·008	0·006	0·024
O(2)	0·198	0·925	0·102	0·009	0·006	0·023
O(3)	0·456	0·982	0·208	0·008	0·006	0·020
O(4)	0·677	0·018	0·885	0·009	0·006	0·026
O(5)	0·858	0·019	0·441	0·008	0·006	0·022
O(6)	0·035	0·112	0·897	0·008	0·006	0·026
O(7)	0·948	0·851	0·093	0·008	0·006	0·024
O(8)	0·239	0·067	0·540	0·008	0·006	0·024
O(9)	0·345	0·824	0·668	0·009	0·006	0·024
O(10)	0·630	0·140	0·292	0·009	0·007	0·025
O(11)	0·686	0·866	0·351	0·009	0·006	0·028
O(12)	0·110	0·209	0·434	0·008	0·005	0·016
O(13)	0·292	0·227	0·134	0·007	0·007	0·021
O(14)	0·469	0·201	0·853	0·008	0·005	0·020
O(15)	0·836	0·235	0·912	0·007	0·007	0·019

Table 3. *Calculated and observed structure factors*

	X-ray data				Neutron data			
hkl	jF_c^2	$\sum_r jF_c^2$	$\sum_r jF_o^2$	*w*	jF_c^2	$\sum_r jF_c^2$	$\sum_r jF_o^2$	*w*
100	.1	.1	.2	.50	2.5	2.5	.8	.62
110	.3	.3	.4	.50	.9	.9	.8	.71
020	6.0	6.0	6.7	.91	9.3	9.3	10.8	.58
120	1.3	1.3	.9	.50	2.5	2.5	1.4	.71
200	8.9	8.9	8.3	.91	15.5	15.5	15.9	.62
210	37.4	37.4	39.8	.63	66.0	66.0	65.9	.45
130	6.7	6.7	6.7	1.00	20.7	20.7	17.0	.72
220	12.5	12.5	10.6	.96	18.1	18.1	11.7	.79
001	5.7	5.7	5.4	1.00	9.2			
$10\bar{1}$	1.0	1.0	.9	.55	5.6	14.8	17.6	.71
011	26.4	26.4	24.9	.71	49.5			
$11\bar{1}$	.2	.2	.9	.55	1.2	50.7	43.5	.60
040	120.3	120.3	120.3	.31	195.2	195.2	196.0	.43
230	13.7	13.7	13.9	.13	8.7	8.7	11.8	.28
101	44.4	44.4	52.0	.13	42.6	42.6	56.0	.32
300	47.0				77.1			
021	12.5	59.5	60.1	.42	52.7			
140	.2				.8			
$12\bar{1}$	.1	.3	1.0	.50	5.6	136.2	141.5	.48
$20\bar{1}$	7.3				37.3			
111	3.1	10.4	8.8	.50	28.5			
310	1.3	1.3	1.0	.83	1.6	67.4	31.4	.20
$21\bar{1}$	.8	.8	1.0	.83	2.0	2.0	1.8	1.00
121	75.4	75.4	82.1	.63	49.8			
320	85.1	85.1	85.8	.56	96.9	146.7	149.6	.60
$22\bar{1}$	205.8	205.8	209.1	.25	104.8	104.8	104.0	.80
031	33.4	33.4	34.7	.42	6.1			
$13\bar{1}$	3.5	3.5	6.6	.25	1.7	7.8	13.5	.33
240	11.7	11.7	12.7	.25	21.2	21.2	17.3	.88
201	3.1	3.1	5.4	.25	1.7	1.7	2.3	.83
211	16.7	16.7	20.9	.50	3.3			
131	.7				12.6			
$30\bar{1}$	.2	.9	2.0	.45	3.5	19.4	15.3	.49
330	.7				8.0			
150	8.1	8.8	8.4	.63	23.4			
$23\bar{1}$	1.0				19.4			
$31\bar{1}$	1.3	2.3	3.4	.83	10.0	60.8	61.8	.32
221	4.1	4.1	4.6	.17	22.6	22.6	17.4	.40
041	11.2				15.2			
$14\bar{1}$	5.9				9.2	24.4	22.3	.41
$32\bar{1}$	.5	17.6	10.2	.50	39.2	39.2	36.7	.41
400	1.9	1.9	4.6	.66	5.5	5.5	6.8	.41
410	28.8	28.8	30.8	.63	25.4			
250	27.7	27.7	23.0	.19	14.4	39.8	31.9	.35
141	45.4	45.4	49.5	.42	68.7	68.7	83.1	.29
340	52.9				42.4			
231	27.4	80.3	65.2	.45	59.7			
$24\bar{1}$	2.5	2.5	9.1	.50	71.2	173.3	169.5	.28
420	7.8				25.3			
$33\bar{1}$	2.1	9.9	6.1	.83	181.3	206.6	196.6	.28
060	3.8				26.7			
301	.7	4.5	6.2	.38	8.9	35.6	35.2	.35
311	3.6				67.5	67.5	75.6	.41
160	7.4	11.0	2.0	.83	15.5	15.5	14.0	.35
$40\bar{1}$	4.3				7.1			
051	7.9	12.2	7.0	.71	28.7			
$15\bar{1}$	4.3	4.3	3.2	.50	51.9			
$41\bar{1}$	11.2	11.2	10.9	.17	41.7	129.4	120.3	.32
321	2.1				35.4			
430	15.4	17.5	11.0	.25	27.9	63.3	68.7	.30
241	6.5	6.5	6.5	.25	65.0	65.0	72.4	.32
151	.9				.6			
$34\bar{1}$	6.7				69.8			
350	.2				27.6			
$42\bar{1}$	20.4	28.2	26.5	.17	110.3	208.3	219.1	.21
$25\bar{1}$	1.7				32.6			
260	16.3	18.0	17.3	.17	107.4	140.0	146.5	.28
331	3.3	3.3	4.0	.25	47.9	47.9	44.4	.34
440	3.6				12.1			
$43\bar{1}$	31.3	34.9	29.3	.63	139.1	151.2	161.0	.31
500	1.2				18.3			
061	6.3	7.5	7.4	.25	31.6	49.9	54.4	.28
251	7.1				7.9			
$16\bar{1}$	.1				31.2			
510	.9	8.1	8.9	.25	175.0	214.1	210.2	.18
170	34.2	34.2	33.7	.56	311.4	311.4	371.1	.28
$35\bar{1}$	15.7				35.3			
401	7.2	22.9	21.6	.25	83.6			
341	6.9	6.9	6.1	.45	35.8	154.7	161.0	.18
411	3.5	3.5	4.7	.45	58.4			
520	1.9				12.9			
161	54.3	56.2	61.2	.17	122.7			
360	69.8				223.2			
$10\bar{2}$	51.7	121.5	106.1	.13	472.8	890.0	854.2	.23
$26\bar{1}$	137.0	137.0	129.4	.17	207.3			
$44\bar{1}$	11.9				82.7			
$11\bar{2}$	1.8				6.5			
$50\bar{1}$	32.7				79.7			
002	2.6	49.0	50.0	.13	.4	376.6	349.6	.17
$51\bar{1}$	4.0				64.6			
421	165.3				243.4			
012	30.0				181.6			
202	3.4	202.7	199.6	.15	39.2	528.8	546.7	.30
450	43.7				59.5			
270	2.0	45.7	44.2	.15	1.5			
$21\bar{2}$	20.2	20.2	23.0	.25	2.5	63.5	64.9	.35
$12\bar{2}$	67.8	67.8	71.6	.17	164.4	164.4	162.0	.39
530	3.1	3.1	2.5	.25	54.6			
$52\bar{1}$	62.4				140.0			
022	6.2	68.6	71.8	.25	29.7	224.3	216.3	.36
102	1.4				4.2			
$22\bar{2}$	7.5	8.9	9.5	.25	8.7			
431	2.7				9.3			
261	6.3	9.0	8.1	.13	24.6			
112	.7				5.6			
351	7.3	8.0	8.2	.13	20.1	72.5	66.5	.19
$36\bar{1}$	.2				12.5			
071	40.0				107.2			
$13\bar{2}$	4.2				24.9			
$30\bar{2}$	.0				40.9			
$17\bar{1}$	7.4	51.8	49.7	.25	21.3	206.9	187.7	.21
$45\bar{1}$	6.3				55.4			
$53\bar{1}$	4.5				60.5			
080	58.7				208.9			
$31\bar{2}$	1.3				1.5			
032	8.7				4.1			
122	4.2	83.7	82.0	.33	15.8	346.2	382.1	.32
540	1.5				40.9			
$23\bar{2}$	8.2	9.7	11.9	.25	4.5	45.4	41.2	.29
180	.9	.9	1.8	.83	12.8			
171	2.1				46.9			
370	.1				7.4			
$32\bar{2}$	2.5	4.7	5.6	.71	13.1	80.2	66.8	.29
$27\bar{1}$	.6				25.1			
460	3.6				4.7			
441	5.4	9.6	11.9	.21	11.7	41.5	45.6	.31
132	4.4				4.3			
202	79.1				174.4			
$14\bar{2}$	58.5	142.0	135.2	.45	177.5	356.2	378.3	.33
212	.4				31.5			
$54\bar{1}$	51.7				69.4			
600	78.9				197.1			
042	6.2				9.9			
501	.3	137.5	141.2	.20	.4	308.3	328.0	.34
610	2.2				21.6			
280	4.3				6.7			
$33\bar{2}$	1.1				15.6			
511	1.7	9.3	9.2	.13	27.5			
561	.4				7.7			
$24\bar{2}$	2.1	2.5	3.1	.25	7.3	86.4	90.6	.26
$40\bar{2}$	73.1				106.5			
222	7.2	80.3	84.9	.50	13.0			
271	32.8	32.8	29.7	.17	29.6			
550	2.7				1.4			
$41\bar{2}$	1.1	3.8	3.1	.17	1.0	151.5	155.7	.40
$46\bar{1}$	11.9				55.6			
$60\bar{1}$	1.9				1.8			
620	4.8	18.6	21.8	.17	6.4			
521	2.1	2.1	3.1	.25	.2	64.0	57.0	.27
$37\bar{1}$	6.0				6.5			
$61\bar{1}$	21.2				78.4			
142	1.5	28.7	27.8	.25	12.6	87.5	102.0	.24
451	.6				34.5			
$42\bar{2}$	5.7				2.2			
081	13.4	19.7	19.6	.25	56.0			
$18\bar{1}$	12.5	12.5	6.1	.25	28.5	121.2	125.2	.35
232	.4				23.9			
$15\bar{2}$	2.8				27.1			
$62\bar{1}$	1.0				1.8			
$34\bar{2}$	1.4	5.6	10.2	.20	13.9	66.7	66.7	.27
$55\bar{1}$	1.4				21.8			
630	1.2	2.6	2.3	.25	24.6			
052	28.4				58.4			
531	2.8	31.2	37.7	.22	7.7	113.5	146.0	.27
470	3.3				66.1			
181	48.7				93.3			
$25\bar{2}$	34.4	86.4	76.8	.20	102.2	261.6	267.3	.24
380	39.7				141.7			
$28\bar{1}$	4.4				15.3			
$43\bar{2}$	2.2				1.9			
302	2.5	48.8	45.9	.13	17.2	176.1	146.5	.19
190	10.3				60.0			
312	.7				36.1			
$63\bar{1}$	32.8	43.9	47.4	.17	50.4	146.5	144.7	.30
560	5.8				27.6			
152	2.2				28.5			
371	5.0				38.0			
242	108.5	121.5	126.6	.25	56.3	150.4	143.7	.27
322	3.3				7.4			
640	118.6				198.0			
541	1.7	123.6	143.3	.13	7.0			
$47\bar{1}$	23.1				47.7			
461	109.6				311.3			
$50\bar{2}$	1.0				53.3			
$35\bar{2}$	4.5	138.2	136.6	.13	103.3	727.9	697.8	.31
290	25.8				35.0			
281	6.1				22.2			
$51\bar{2}$	.2	32.1	23.0	.10	9.1			
$44\bar{2}$	108.8				89.2			
$16\bar{2}$	47.1	155.9	154.0	.17	96.0	251.5	225.5	.24
$38\bar{1}$	8.9				35.6			
$56\bar{1}$	40.5				126.5			
$64\bar{1}$	5.0				47.5			
062	3.8	58.2	52.7	.25	13.1	222.7	224.5	.34
332					83.2			
$52\bar{2}$					23.0			
$26\bar{2}$					.8	107.0	109.7	.24
252					8.3			
601					82.6			
091					11.1			
$19\bar{1}$					116.9	218.9	233.7	.35
611					22.8			
480					10.2			
650					60.3			
551					31.4			
162					47.0			
700					.8			
$53\bar{2}$					4.1	176.6	127.4	.23
710					.0			
570					14.4			
191					2.8			
$45\bar{2}$					14.2			
621					66.6			
342					7.8			
390					34.7			
$70\bar{1}$					.0			
$36\bar{2}$					19.7			
$29\bar{1}$					52.1	212.3	234.6	.24
402					4.1			
$71\bar{1}$					16.9			
$65\bar{1}$					1.1			
0.10.0					15.8			
381					68.6			
720					12.2			
412					115.0			
471					19.5	253.2	237.7	.24
1.10.0					28.8			
$48\bar{1}$					13.4			
$17\bar{2}$					14.7			
$72\bar{1}$					13.0	69.9	67.2	.24
631					44.7			
422					30.3			
$57\bar{1}$					36.4			
$54\bar{2}$					1.2			
072					22.8	135.4	126.9	.24
$27\bar{2}$					158.2			
730					6.2			
262					82.4			
291					94.8			
$60\bar{2}$					51.1	392.6	364.9	.23
660					19.0			
561					19.0			
$61\bar{2}$					161.9			
352					66.3			
391					76.9			
$73\bar{1}$					27.0			
2.10.0					61.8	431.9	468.2	.22
432					57.4			
172					67.5			
$46\bar{2}$					23.1	148.0	170.8	.24
622					2.8			
641					56.5			
$66\bar{1}$					75.6	134.9	129.5	.24
372					66.5	66.5	77.5	.24
740					53.1			
490					10.5			
$55\bar{2}$					.1			
580					26.0			
0.10.1					61.1			
$1.10.\bar{1}$					16.1	166.9	147.8	.21
$74\bar{1}$					41.2			
$63\bar{2}$					25.9	67.1	79.5	.24
442					106.5			
481					55.6	162.1	164.7	.24

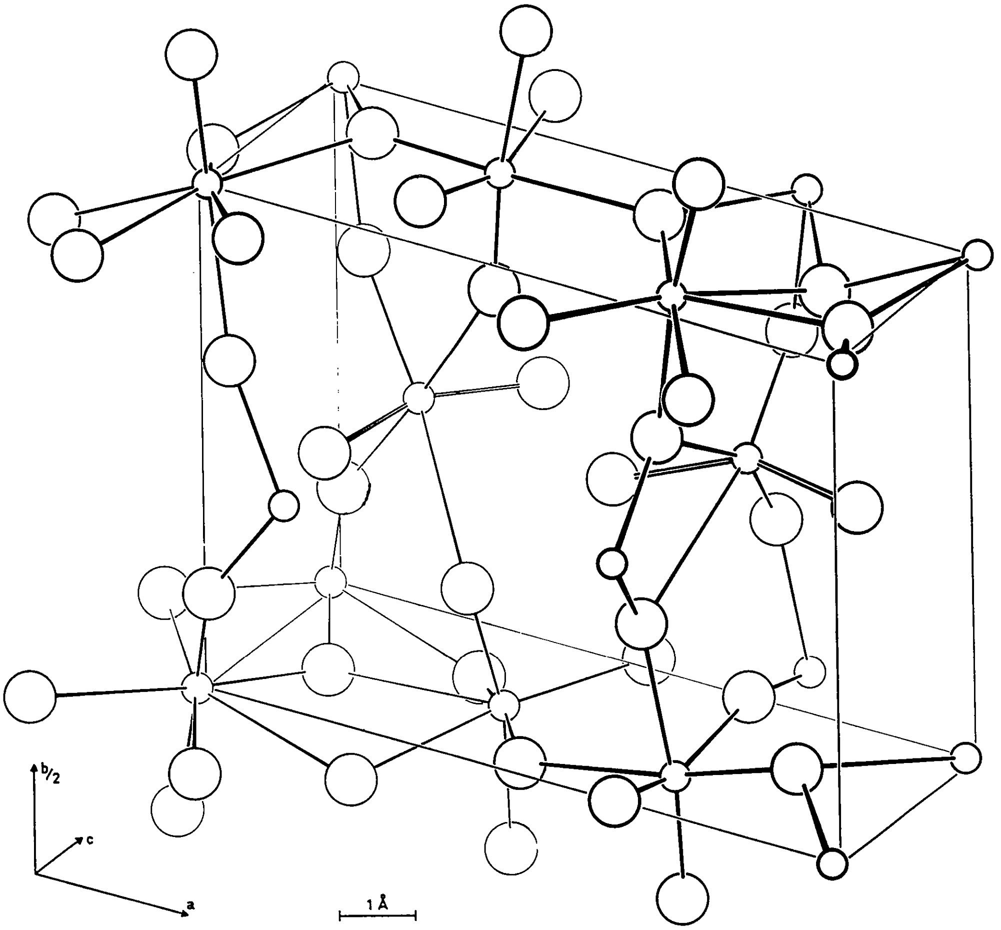

Fig. 1. A perspective drawing of the structure; small circles designate uranium atoms and large circles oxygen atoms. The volume outlined is one half of the unit.

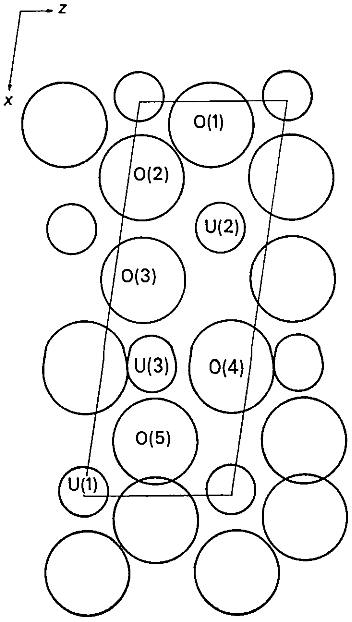

Fig. 2. A projection, along the y axis, of the cell contents between $y=-0{\cdot}07$ and $y=+0{\cdot}02$. Small circles designate uranium atoms, large circles oxygen atoms.

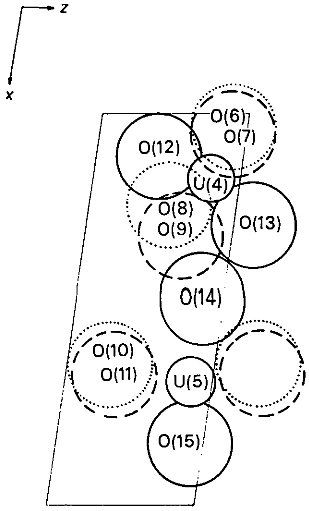

Fig. 3. A projection, along the y axis, of the cell contents between $y=0{\cdot}07$ and $y=0{\cdot}37$. Small circles designate uranium atoms, large circles oxygen atoms. Full circles have y parameters between 0·20 and 0·26; dashed circles between 0·32 and 0·37; dotted circles between 0·07 and 0·14.

Table 5. U–O *distances* (Å) *smaller than* 3 Å

U(1)–O(1)	2·07	0·11	U(2)–O(1)	2·72	0·09	U(3)–O(3)	2·16	0·09	U(4)–O(6)	2·24	0·09	U(5)–O(9′)	2·11	0·10
–O(1)	2·21	0·11	–O(2)	2·40	0·10	–O(4)	1·79	0·11	–O(7′)	2·19	0·09	–O(9′)	2·27	0·10
–O(2)	2·39	0·09	–O(2)	2·49	0·10	–O(4)	2·17	0·11	–O(8)	2·69	0·10	–O(10)	2·46	0·10
–O(5)	2·37	0·10	–O(3)	2·31	0·09	–O(5)	1·98	0·09	–O(11′)	2·60	0·10	–O(10)	2·77	0·10
–O(5)	2·40	0·10	–O(3)	2·42	0·09	–O(10)	2·09	0·11	–O(12)	1·52	0·08	–O(14)	2·28	0·09
–O(6)	1·74	0·08	–O(8)	1·69	0·10	–O(11)	1·88	0·09	–O(13)	1·65	0·09	–O(15)	1·67	0·08
–O(7)	2·22	0·08	–O(9)	2·10	0·10									

$\frac{1}{2}$ by the atoms O(6), O(7), O(8), O(9), O(10) and O(11). The lengths of the various U–O bonds are shown in Table 5.

Owing to the poor crystallinity of the samples the diffraction peaks were broadened appreciably. In order to obtain a sufficient number of intensities it was therefore necessary to separate partly overlapping peaks, even if this could not be done very accurately. This, together with the unfavourable ratio of measured intensities and parameters, inevitably leads to the high standard deviations as given in Tables 4 and 5. Even so, six O–O distances are too small, deviating by more than one standard deviation from the expected minimum value of 2·5 Å. In only one case, however, is the deviation more than twice the standard deviation, *viz.* O(1)–O(5) (2·21 ± 0·12 Å). The average value for the 42 O–O distances smaller than 3 Å is 2·70 Å.

As regards coordination of the uranium atoms by oxygen, three different cases can be distinguished.

(*a*) U(4) and U(5). These have six oxygen neighbours, two of which can be considered to form a uranyl group, *viz.* O(12) and O(13) with U(4), and O(14) and O(15) with U(5). The angles between the U–O bonds of the uranyl groups are 152 ± 4° and 148 ± 4° at U(4) and U(5) respectively, deviating considerably from the expected value of 180°. Three uranyl bonds are approximately of correct length, according to Zachariasen (1954). The fourth, U(5)–O(14), is much longer.

(*b*) U(3) is coordinated by six oxygen atoms which form a deformed octahedron.

(*c*) U(1) and U(2) have seven oxygen neighbours at distances of 2·7 Å or less. The O(4) atom also plays some role in the coordination of both uranium atoms, but at distances of 3·2 and 3·6 Å from U(1) and U(2) respectively. An attempt to consider the position of this atom as the centre of gravity of two positions, each with a weight of one half, led to a negative result.

Fig. 2 is a projection, along the y axis, of the cell contents between $y = -0{\cdot}07$ and $y = +0{\cdot}02$. A comparison with Fig. 1 should give a clear idea of the coordination of the atoms U(1), U(2) and U(3). As has already been mentioned under *Experimental*, β-UO_3 recrystallizes at elevated temperatures to the γ modification. γ-UO_3 consists of chains of six-coordinated uranium atoms, all lying in parallel planes and interconnected by uranium atoms with seven-coordination (Engmann & de Wolff, 1963). The atomic arrangement in this structure is markedly different from that in β-UO_3. There is, however, one remarkable similarity: both structures contain uranium atoms with different coordinations and different functions. It is highly probable that this is also the case in ε-UO_3, which has a triclinic unit cell with 8 molecules (Kovba, Vidavskii & Lavut, 1963) and in α-UO_3, the structure of which is more complex than was thought until recently (Loopstra & Cordfunke, 1966). This would mean that only cubic δ-UO_3 (Wait, 1955) does not contain more than one kind of uranium atom, if at least its proposed structure is correct.

The author wishes to express his gratitude to Dr E. H. P. Cordfunke and his staff for preparing the samples, to Dr H. M. Rietveld for his help in the computing problems and to Dr B. O. Loopstra for his interest and much helpful critisicm.

References

Cordfunke, E. H. P. & Aling, P. (1965). *Trans. Faraday Soc.* **61**, 50.

Cromer, D. T. & Waber, J. T. (1964). LAMS-3056.

Debets, P. C. (1964). *J. Inorg. Nucl. Chem.* **26**, 1469.

Engmann, R. & de Wolff, P. M. (1963). *Acta Cryst.* **16**, 993.

Kovba, L. M., Vidavskii, L. M. & Lavut, E. G. (1963). *Zh. Strukt. Khim.* **4**, 627.

Loopstra, B. O. & Cordfunke, E. H. P. (1966). *Rev. Trav. chim. Pays-Bas.* **85**, 135.

Rietveld, H. M. (1966). *Acta Cryst.* **20**, 508.

Wait, E. (1955). *J. Inorg. Nucl. Chem.* **1**, 309.

Zachariasen, W. H. (1954). *Acta Cryst.* **7**, 795.