

## Neutron Powder Profile Studies of the Gamma Uranium Trioxide Phases

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Neutron powder profile studies show the existence of three phases in gamma uranium trioxide between 373°K and 77°K. The three phases are closely related and the transitions smooth and displacive. At 373°K,  $\gamma$ - $\text{UO}_3$  is tetragonal, with  $a = 6.9013$  (5) and  $c = 19.9754$  (18) Å, and space group  $I4_1/amd(D_{4h}^{19})$ . At 323°K,  $\gamma$ - $\text{UO}_3$  becomes orthorhombic, space group  $F_{ddd}(D_{2h}^{24})$ , with the cell dimensions (293°K)  $a = 9.787$  (3),  $b = 19.932$  (4) and  $c = 9.705$  (3) Å. There is a further transition between 293°K and 77°K, and, at 77°K, the orthorhombic dimensions of the pseudocell are  $a = 9.8225$  (7),  $b = 19.8487$  (15), and  $c = 9.6318$  (7) Å. The neutron diffraction studies show that, in all three phases, the coordination polyhedra of the two crystallographically distinct uranium atoms are octahedral and (dodecahedral-2) respectively. At 293°K, the shortest U-O distance is 1.796 (6) Å, and thus there are no pure uranyl bonds, in agreement with the infrared spectrum. The U-O distances are precise to about  $\pm 0.006$  Å, about ten times the precision of an earlier X-ray single-crystal study, in which the conclusions were in conflict with the infrared spectrum. The structure is made up of parallel chains of edge-fused U(2) octahedra, cross-linked by U(1) dodecahedra. The atomic shifts are not great in going from 373°K to 77°K; at 293°K the data will refine in the pseudotetragonal cell as well as the true orthorhombic cell, and the 77°K data will refine in the  $F_{ddd}$  cell.

### Introduction

The oxides  $\text{UO}_3$  show a great variety of structural patterns;  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ - $\text{UO}_3$  are known, as well as a high pressure form (1). A tentative phase diagram for the  $\text{UO}_3/\text{U}_3\text{O}_8$  system has been given (2). Engmann and de Wolff (3) determined the basic structure of  $\gamma$ - $\text{UO}_3$  from X-ray powder photographs, in the tetragonal space group  $I4_1/amd(D_{4h}^{19})$ . Line splittings in their photographs indicated that, at room temperature, the structure was really of lower symmetry, but strongly pseudotetragonal.

Siegel and Hoekstra (4) studied  $\gamma$ - $\text{UO}_3$  by X-ray single-crystal diffraction and found the true unit cell to be orthorhombic,  $F_{ddd}(D_{2h}^{24})$ , with twice the volume of the tetragonal cell. The orthorhombic cell retained the long 20 Å  $c$ -repeat of the tetragonal cell, but the

other two orthorhombic cell edges were diagonals of the tetragonal basal plane (see Table I for unit cell data). They refined a model in the orthorhombic cell differing only slightly from the tetragonal model.

They concluded the two independent uranium atoms, U(1) and U(2) were both octahedrally coordinated by oxygen atoms. A major difficulty with this interpretation was that it could not be reconciled with the infrared spectrum (4) which showed the absence of strong uranyl bonds of length  $\sim 1.70$  Å. In the single crystal X-ray study (4) collinear bonds U(1)-O(3) of length 1.79 (6) Å appeared to be uranyl bonds. In the X-ray studies, the geometry of the coordinated oxygens could not be examined in detail because of the low accuracy in the oxygen positions.

Because it was obvious the oxygen positions would have to be more precisely determined in order to interpret the bonding patterns in  $\gamma$ - $\text{UO}_3$ , the present series of neutron diffrac-

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TABLE I

UNIT CELL DIMENSIONS<sup>a</sup> FOR TETRAGONAL ( $I4_1/amd$ ) AND ORTHORHOMBIC ( $F_{ddd}$ ) GAMMA  $UO_3$  (P = Petten, LH = Lucas Heights)

Data	Crystal system	$a$ (Å)	$b$ (Å)	$c$ (Å)	$U$ (Å <sup>3</sup> )	$Z$	$D_x$ (g cm <sup>-3</sup> )
373°K, P	Tetragonal	6.9013 (5)	=a	19.9754 (18)	951.4 (2)	16	7.99
293°K, LH	Pseudotetragonal	6.8920 (14)	=a	19.9290 (48)	946.6	16	8.03
293°K, Ref. (3)	Pseudotetragonal	6.89	=a	19.94	946.6	16	8.03
293°K, Ref. (4)	Orthorhombic	9.813 (8)	19.93 (8)	9.711 (8)	1899.2	32	8.00
293°K, LH	Orthorhombic	9.787 (3)	19.932 (4)	9.705 (3)	1893.3 (10)	32	8.03
77°K, P	Pseudo- $F_{ddd}$	9.8225 (7)	19.8487 (15)	9.6318 (7)	1877.9 (4)	—	—
77°K, LH	Pseudo- $F_{ddd}$	9.821 (4)	19.868 (8)	9.654 (4)	1884 (2)	—	—

<sup>a</sup> Cell dimension errors do not include errors in the wavelengths.

tion studies on  $\gamma$ - $UO_3$  was undertaken. It was thought that this technique, with the powerful profile analysis method of Rietveld (5) would give the required precision.

It was also thought that, since the room temperature structure was nearly tetragonal, it would become truly tetragonal at higher temperatures. Guinier-Lenné photographs taken by one of us (B. O. L.) showed this to be the case and the transition temperature to be about 323°K. Thus, neutron diffraction data were collected at 373°K (Petten), 293°K (Lucas Heights and Petten) and 77°K (Lucas Heights and Petten). The analysis of these data, and the resulting conclusions about the structure of  $\gamma$ - $UO_3$  are presented in this paper.

## Experimental

The Lucas Heights  $\gamma$ - $UO_3$  sample was prepared by reacting  $U_3O_8$  and oxygen at 823°K and 6.9 MPa for 48 hours in a stainless steel autoclave. A Guinier photograph showed the sample was pure, and gave the same line splittings as observed by Engmann and de Wolff (3). The sample was kept away from atmospheric moisture at all times because of its slow reaction giving  $UO_3 \cdot 2H_2O$ . The Petten sample was prepared by heating uranyl nitrate hexahydrate first at 470°K until dry; thereafter it was powdered and heated very slowly to about 770°K in air or oxygen.

The Lucas Heights neutron patterns were taken at 293°K and 77°K with the elastic diffraction technique (6), a wavelength of

1.085 Å, steps of  $0.1^\circ 2\theta$  and a monitor setting of  $10^5$ . The sample was enclosed in a quartz tube for the 293°K run and in a Kel-F tube for the 77°K run. The complete background intensity was included in the Rietveld weighting scheme.

The Petten neutron patterns were taken at 373°K (monitor,  $535 \times 10^3$ ) and 77°K with  $\lambda = 2.565$  Å, with steps of  $0.18^\circ 2\theta$  for the 373°K pattern and  $0.072^\circ 2\theta$  for the 77°K pattern. The 77°K pattern was the sum of three separate runs with monitor settings between  $130 \times 10^3$  and  $270 \times 10^3$ . The collimation conditions were (no  $\alpha_2$  slit):  $\alpha_1$  and  $\alpha_3 = 30'$  for the 373°K pattern and  $\alpha_1$  and  $\alpha_3 = 10'$  for the 77°K pattern. In the tables in this paper, the Petten data is denoted by a P and the Lucas Heights data by LH.

## Neutron Profile Refinements

### (a) Refinement of Tetragonal 373°K Data and Refinement of the 293°K Data in the Tetragonal Space Group

The Guinier-Lenné photograph showed that the tetragonal-orthorhombic transition at 323°K was smooth and displacive. The 293°K data were therefore refined with the tetragonal pseudocell, although the structure was actually just below the transition, in the orthorhombic region. This was done in order to check on the departure from tetragonal symmetry just below the transition.

The profile refinements were carried out with the Rietveld (5) program, with the neutron

scattering lengths (7)  $b_U = 8.5$  fm and  $b_O = 5.8$  fm. The positional parameters for the refinements in  $I4_1/amd$  for the 373°K and 293°K data are compared with the original tetragonal cell coordinates of Engmann and de Wolff (3) in Table II (to preserve consistency with the orthorhombic  $F_{dd}$  cell, the original (3) nomenclature for the oxygen atoms has been changed).

The neutron positional parameters in the true tetragonal cell at 373°K and the pseudo-tetragonal cell at 293°K agree very closely, Table II. Thus, the orthorhombic structure at 293°K is only a very slight distortion from tetragonal symmetry. The original positions of Engmann and de Wolff (3) were essentially correct, but in error by up to 0.26 Å.

The residuals

$$R_1 = \sum \left| y_0 - \frac{1}{c} y_c \right| / \sum |y_0|,$$

$$R_2 = \left( \sum w \left( y_0 - \frac{1}{c} y_c \right)^2 / \sum w y_0^2 \right)^{1/2},$$

$$R_3 = \sum \left| I_0 - \frac{1}{c} I_c \right| / \sum I_0,$$

$$R_{\text{expected}} = ((\text{NO}-\text{NV}) / \sum w y_0^2)^{1/2}$$

and

$$\chi^2 = \sum w \left( y_0 - \frac{1}{c} y_c \right)^2 / (\text{NO}-\text{NV})$$

are given in Table III. The symbols have their usual meanings (5). The  $y$ 's are pattern counts corrected for background, and the  $I$ 's are integrated intensities for the ( $hkl$ ) lines. The observed and calculated profiles for the 373°K data are given in Fig. 1.

(b) *Refinement of 293°K Data in the True Orthorhombic Cell*

$\gamma$ - $\text{UO}_3$  is orthorhombic at 293°K with space group  $F_{dd}$ , and the cell dimensions in Table I. The orthorhombic cell is related to the tetragonal cell as follows. The tetragonal 20 Å repeat is preserved, (orthorhombic  $b$ -axis) but the orthorhombic  $a$ - and  $c$ -axes are diagonals of the tetragonal basal plane. At the transition point,

$$a_{\text{ortho}} = c_{\text{ortho}} = \sqrt{2} a_{\text{tetra}}$$

and

$$b_{\text{ortho}} = c_{\text{tetra}}$$

TABLE II

POSITIONAL PARAMETERS FOR  $\gamma$ - $\text{UO}_3$  IN THE TRULY TETRAGONAL PHASE AT 373°K, COMPARED WITH (a) THE POSITIONAL PARAMETERS FROM THE PSEUDOTETRAGONAL CELL REFINEMENT OF THE 293°K DATA, AND (b) THE ORIGINAL PARAMETERS OF ENGMANN AND DE WOLFF (3). ALL  $x$ -COORDINATES ARE ZERO.

Atom	$10^4 y$	$10^4 z$	$B(\text{Å}^2)$	Data set
U(1)	2500	0618(3)	1.42(11)	373°K, P
	2500	0621(2)	0.62(12)	293°K, LH
	2500	0600		293°K, Ref. (3)
U(2)	0000	5000	1.42(11)	373°K, P
	0000	5000	0.15(10)	293°K, LH
	0000	5000		293°K, Ref. (3)
O(1)	9476(7)	4073(3)	1.96(11)	373°K, P
	9487(8)	4076(3)	0.74(14)	293°K, LH
	9430	4060		293°K, Ref. (3)
O(2)	0496(7)	2645(3)	1.96(11)	373°K, P
	0482(8)	2652(3)	0.97(17)	293°K, LH
	0390	2640		293°K, Ref. (3)
O(3)	5100(8)	0660(3)	1.96(11)	373°K, P
	5103(10)	0666(4)	2.00(14)	293°K, LH
	5470	0700		293°K, Ref. (3)

TABLE III  
*R*-FACTORS AND  $\chi^2$  VALUES FOR THE REFINEMENTS OF THE 373°K AND 293°K DATA IN THE TETRAGONAL SPACE  
 GROUP  $I4_1/amd$

Data	$R_1$	$R_2$	$R_3$	$R_{\text{expected}}$	NO	NV	$\chi^2$
Truly tetragonal, 373°K data	0.063	0.073	0.097	0.035	398	16	7.7
Pseudotetragonal, 293°K data	0.103	0.117	0.067	0.061	606	19	3.7

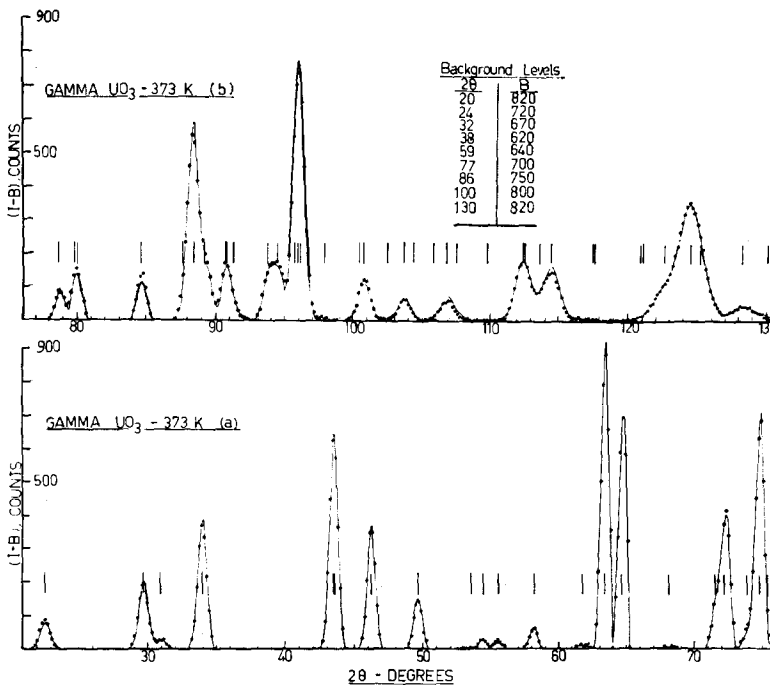


FIG. 1. Observed and calculated neutron powder diffraction profiles for the tetragonal phase of  $\gamma$ - $\text{UO}_3$  at 373°K (Petten data).

The orthorhombic coordinates are related to the tetragonal coordinates by the formulas:

$$x_{\text{ortho}} = 0.25 - 0.5 x_{\text{tetra}} + 0.5 y_{\text{tetra}}$$

$$y_{\text{ortho}} = z_{\text{tetra}}$$

$$z_{\text{ortho}} = 0.25 + 0.5 x_{\text{tetra}} + 0.5 y_{\text{tetra}}$$

The parameters from the profile refinement of the 293°K data are given in Table IV, where they are compared with the X-ray coordinates of Siegel and Hoekstra (4).

Table IV shows that the errors in the neutron profile refinement are up to 10 times less than the errors in the X-ray study, although the

X-ray parameters are essentially correct. The large X-ray errors caused the difficulties in interpreting the X-ray results.

For a strictly tetragonal structure, the orthorhombic  $x$  and  $z$  coordinates should be identical for each atom. It is seen in Table IV there are significant differences, the largest being for O(3), where  $x$  O(3) = -0.0001(12) and  $z$  O(3) = -0.0096(13). This is a significant deviation from tetragonal symmetry.

The  $R$ -factors for the refinement of the neutron data at 293°K were  $R_1 = 0.083$ ,  $R_2 = 0.098$ ,  $R_3 = 0.056$ , and  $R_{\text{expected}} = 0.062$ . NO, NV and  $\chi^2$  were 553, 23 and 2.5, the last

TABLE IV

STRUCTURAL PARAMETERS FROM THE NEUTRON PROFILE REFINEMENT OF THE 293°K DATA IN THE TRUE ORTHORHOMBIC CELL, COMPARED WITH THE SINGLE CRYSTAL X-RAY PARAMETERS OF SIEGEL AND HOEKSTRA (4)

Atom	Data	$10^4 x$	$10^4 y$	$10^4 z$	$B(\text{\AA}^2)$
U(1)	293°K, LH	1250	3115(3)	1250	0.98(12)
U(1)	X-ray Single Crystal (4)	1250	3121(1)	1250	1.15(7)
U(2)	293°K, LH	5000	5000	5000	0.45(9)
U(2)	X-ray Single Crystal (4)	5000	5000	5000	1.19(7)
O(1)	293°K, LH	0261(12)	4081(3)	0258(12)	1.32(15)
O(1)	X-ray Single Crystal (4)	0290(30)	4080(20)	0310(30)	1.40(70)
O(2)	293°K, LH	-0284(12)	2652(3)	-0205(12)	1.13(15)
O(2)	X-ray Single Crystal (4)	-0244(65)	2700(30)	-0330(60)	3.10(110)
O(3)	293°K, LH	-0001(12)	-0663(3)	-0096(13)	1.96(14)
O(3)	X-ray Single Crystal (4)	-0030(60)	-0670(30)	-0070(60)	3.20(110)

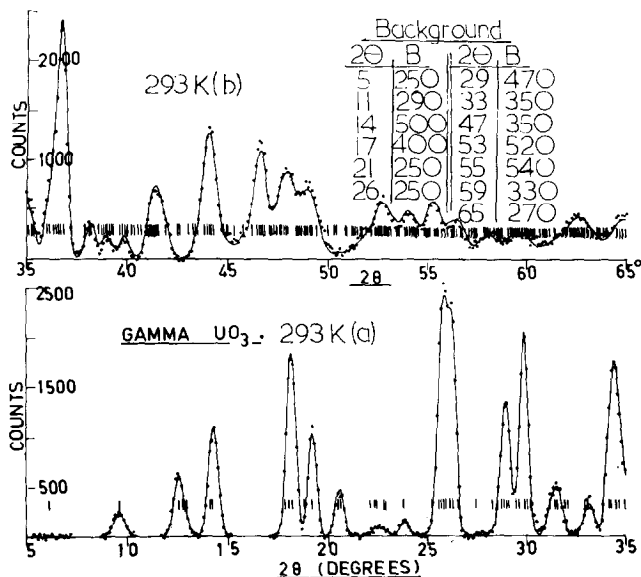


FIG. 2. Observed and calculated neutron powder profiles for orthorhombic  $\gamma$ - $\text{UO}_3$  at 293°K (Lucas Heights data).

residual showing that the orthorhombic structure gave a better fit to the data than the pseudotetragonal refinement, for which  $\chi^2$  was 3.7 (Table III). The observed and calculated profiles at 293°K are given in Fig. 2. A refinement was also carried out for a pattern collected at Petten at 293°K, but as the results were identical with the Lucas Heights results, they are not presented here.

(c) *Refinement of Data at 77°K collected at Petten and Lucas Heights*

Refinement of data sets at 77°K collected independently and with different samples at Petten and Lucas Heights gave identical, but unexpected, results. The Lucas Heights data were refined in  $F_{aaa}$  and gave a higher  $R$ -factor than expected with some regions of the pattern

not showing a good fit. Some small peaks in the pattern, which could not be impurities (the room temperature refinement showed the sample was pure), were not fitted by the model. The same result was obtained with the Petten data. The set of small peaks which could not be fitted were of the same  $d$ -spacings as those in the Lucas Heights data.

This was evidence that a further phase change occurs in  $\gamma$ - $\text{UO}_3$  between 293°K and 77°K. The transition was again displacive as the 77°K data were fitted reasonably well with the orthorhombic  $F_{ddd}$  model and coordinates derived in this way agreed with the parameters at 293°K in Table V. The analysis of the Petten data at 77°K is presented here, as this data is

TABLE V

POSITIONAL PARAMETERS FOR THE  $F_{ddd}$  REFINEMENT OF THE PETTEN 77°K DATA FOR  $\gamma$ - $\text{UO}_3$ , COMPARED WITH THE PARAMETERS FOR THE 293°K  $F_{ddd}$  REFINEMENT (LUCAS HEIGHTS DATA)

Atom	Data	$10^4 x$	$10^4 y$	$10^4 z$	$B(\text{\AA}^2)$
U(1)	77°K, P	1250	3123(3)	1250	1.07(14)
U(1)	293°K, LH	1250	3115(3)	1250	0.98(12)
U(2)	77°K, P	5000	5000	5000	1.07(14)
U(2)	293°K, LH	5000	5000	5000	0.45(9)
O(1)	77°K, P	0234(8)	4071(3)	0298(7)	0.96(13)
O(1)	293°K, LH	0261(12)	4081(3)	0258(12)	1.32(15)
O(2)	77°K, P	-0329(7)	2655(3)	-0221(7)	0.96(13)
O(2)	293°K, LH	-0284(12)	2652(3)	-0205(12)	1.13(15)
O(3)	77°K, P	0063(7)	-0632(3)	-0123(8)	0.96(13)
O(3)	293°K, LH	-0001(12)	-0663(3)	-0096(13)	1.96(14)

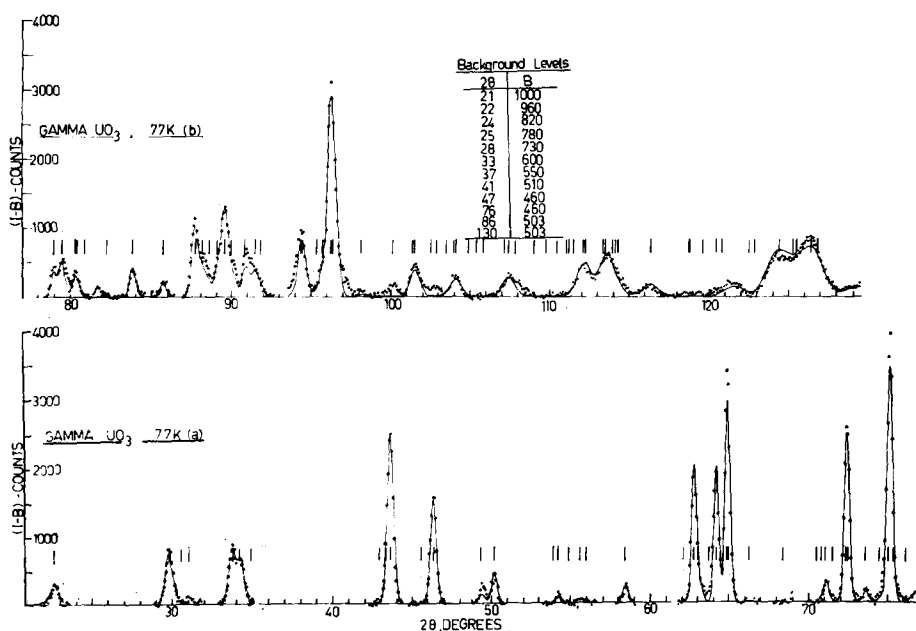


FIG. 3. Observed and calculated neutron powder profiles for  $\gamma$ - $\text{UO}_3$  at 77°K (Petten data, refinement in pseudo-orthorhombic cell,  $F_{ddd}$ ).

of higher resolution and shows the extra peaks in more detail.

The positional parameters for the  $F_{ada}$  refinement of the 77°K data are compared with the 293°K  $F_{ada}$  parameters in Table V.

It is seen from Table V that O(3) deviates markedly from tetragonal symmetry at 77°K, since  $x$  O(3) = 0.0063(7) and  $z$  O(3) = -0.0123(8). The deviations of O(1) and O(2) are not so marked. The observed and calculated profiles at 77°K (Fig. 3), show positive peaks unaccounted for by the orthorhombic  $F_{ada}$  structure, and the  $R$ -factors at 77°K are much higher than the statistically expected  $R$ -factor:

$R_1 = 0.110$ ,  $R_2 = 0.182$ ,  $R_3 = 0.191$  and  $R_{\text{expected}} = 0.078$ . The  $\chi^2$  value was 5.98. It is possible that the true cell at 77°K is still orthorhombic, as the profile refinement gave low errors in the orthorhombic  $F_{ada}$  cell edges Table I. The  $d$ -spacings of the extra lines suggested that the  $a$ -axis of the orthorhombic cell should be doubled. A full analysis of the 77°K pattern will be presented at a later date.

Refinement carried out excluding the regions of the extra peaks did not give a significant reduction in the  $R$ -factors. Thus, the misfit of the  $F_{ada}$  model was in the main reflexions as well as in the new smaller peaks. Obviously a related structure of lower symmetry must be postulated at 77°K, just as a new structure was required on going from 373 to 293°K.

## Discussion

The structure of  $\gamma$ - $\text{UO}_3$  is best described initially in terms of the basic tetragonal structure at 373°K. The structure is complex, with 16  $\text{UO}_3$  units in the tetragonal cell, and because of this, the overall structure has never been adequately illustrated. The difficulty in presenting the structure, together with the low accuracy in the oxygen positions in the previous X-ray studies, has led to confusion as to the type of bonding around U(1) and U(2). The view down the tetragonal  $a_2$  axis is shown in Fig. 4, where the distances of the atoms from the plane of the paper are given in hundredths of  $a_2$ .

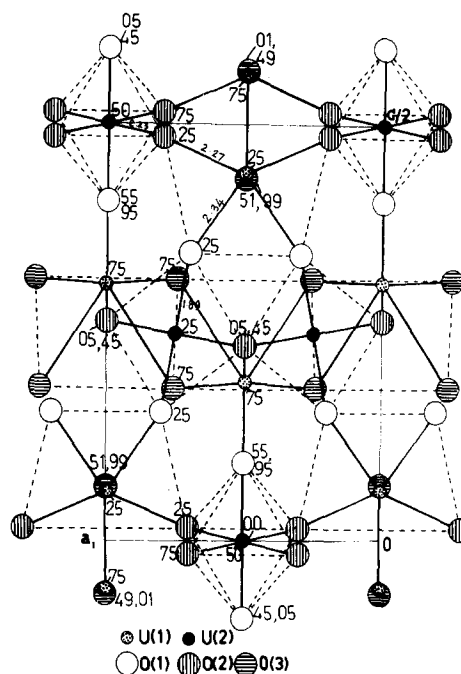


FIG. 4. The structure of  $\gamma$ - $\text{UO}_3$  seen down the  $a_2$  axis of the tetragonal cell. Coordinates of the atoms from the paper in hundredths of  $a_2$  are given.

### (a) The Coordination Polyhedron around U(2)

This is a slightly distorted octahedron. U(2) is surrounded by two O(1) and four O(2) atoms, and the octahedra form endless chains by sharing O(2)–O(2) edges. The chains run parallel to  $a_1$  or  $a_2$ , depending on the height of the chain along  $c$ . Thus, chains running parallel to  $a_2$  along the lines  $(o, y, \frac{1}{2})$  and  $(\frac{1}{2}, y, o)$  are seen end-on, and a chain parallel to  $a_1$  along  $(x, \frac{1}{4}, \frac{1}{4})$  is seen side-on in Fig. 4. Inspection of the latter chain shows that the octahedra are alternately tilted slightly in opposite directions about [001] to allow bridging of the apical O(1) atoms to U(1) atoms at the same  $y$ -level, above and below the octahedra in the  $c$ -direction. The chains seen end-on similarly bridge to U(1) atoms in the same  $x$ -level as the U(2) atoms through O(1) atoms.

The bond lengths and angles around U(2) are given in Table VI. As the U(2) octahedron has a centre of symmetry, all the O–U(2)–O diameters are linear. There is some distortion

TABLE VI  
BOND LENGTHS AND ANGLES IN GAMMA  $\text{UO}_3$ \*

Bond or Angle (Å or deg.)	373°K, P (a)	Ref. (3), X-ray (b)	293°K, LH (c)	Ref. (4), X-ray (d)	77°K, P (e)
U(2)–O(1)(2x)	1.887(5)	1.91(10)	1.866(5)	1.88(4)	1.880(7)
U(2)–O(2)(2x)	2.230(3)	2.27(10)	2.205(12)	2.16(6)	2.165(7)
U(2)–O(2)(2x)		2.27(10)	2.266(13)	2.27(6)	2.240(7)
U(1)–O(1)(2x)	2.344(6)	2.34(10)	2.361(6)	2.32(4)	2.319(8)
U(1)–O(2)(2x)	2.274(5)	2.19(10)	2.262(6)	2.28(6)	2.298(7)
U(1)–O(3)(2x)	1.796(6)	2.06(10)	1.796(6)	1.79(6)	1.763(7)
U(1)–O(3)(2x)	3.045(6)		3.041(6)	3.06	3.009(7)
O(2)–U(2)–O(2)(2x)	76.7(2)		76.8(2)		75.1(2)
O(2)–U(2)–O(2)(2x)	103.3(2)		103.2(2)		104.9(2)
O(1)–U(2)–O(2)(2x)	91.2(2)		91.0(4)		91.9(3)
O(1)–U(2)–O(2)	88.8(2)		89.0(4)		88.1(3)
O(1)–U(2)–O(2)			89.3(4)		90.2(3)
O(1)–U(2)–O(2)	91.2(2)		90.7(4)		89.8(3)
All O–U(2)–O diameters are 180°					
O(3)–U(1)–O(3)	174.6(5)		173.9(6)		178.8(7)
O(3)–U(1)–O(3)(2x)	59.7(3)		60.0(3)		56.9(3)
O(3)–U(1)–O(3)	65.9(3)		66.2(2)		68.2(3)
O(1)–U(1)–O(2)(2x)	79.0(2)		78.7(2)		78.1(2)
O(1)–U(1)–O(1)	71.2(3)		70.8(3)		71.5(4)
O(2)–U(1)–O(2)	130.8(3)		131.9(3)		132.2(4)

\* (a) The tetragonal phase at 373°K; (b) from the X-ray study of Engmann and de Wolff (3); (c) the orthorhombic phase at 293°K; (d) from the X-ray study of the orthorhombic phase (4); (e) the 77°K phase, as refined in  $F_{aaa}$ .

of the O(2)–U(2)–O(2) angles in the equatorial plane from 90° due to the edge-fusing by O(2). However, the O(1)–U(2)–O(2) angles are little removed from 90°, even though the O(1) atoms form strong bridges to U(1) atoms. The U(2)–O(1) distance (1.887(5) Å in the tetragonal phase) is lengthened from the uranyl distance, 1.70 Å by the bridging to U(1). The dimensions in Table VI support the view that U(2) is truly octahedral, and distortions can be readily explained by the bridging to nearby U(1) and U(2) atoms.

(b) *The Coordination Polyhedron around U(1)*

The arrangement around U(1) is not so simply explained. Figure 5 shows that the U(1) atoms serve to bridge the chains of U(2)-based octahedra. In Fig. 5, the structural building-block is shown. Parallel chains of U(2)-based octahedra bridged by U(1)-based

polyhedra occur. The blocks in adjacent  $c$ -levels are rotated by 90° about the tetragonal  $c$ -axis, and there is bridging also in the  $c$ -direction (cf. Fig. 4).

Figures 4 and 5 show that U(1) is surrounded by eight oxygen atoms, four in each of two mutually perpendicular planes parallel to the tetragonal  $c$ -axis.

Table VI shows that U(1)–O bonds are divided into four sets of two equivalent bonds, the shortest set being U(1)–O(3)(2x) = 1.796(6) Å and the longest U(1)–O(3)(2x) = 3.045(6) Å. The latter two were neglected in the previous X-ray studies where the arrangement around U(1) was considered to be octahedral. It is shown below that the O(3) atoms at 3.045 Å from U(1) are definitely part of the coordination polyhedron around U(1), and the true coordination number for U(1) is eight.



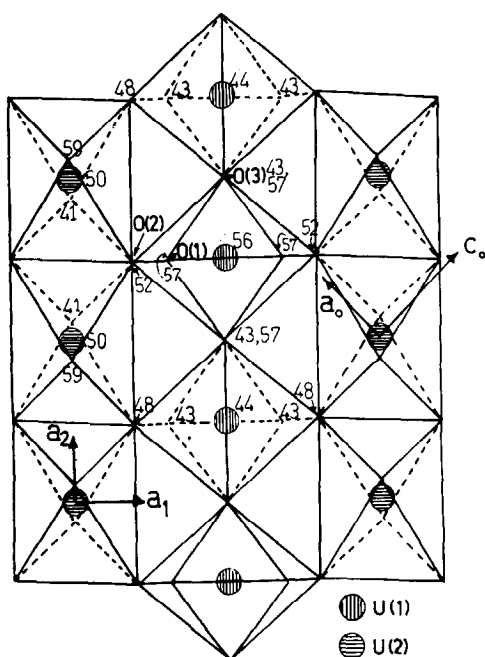


FIG. 5. Part of the structure of  $\gamma$ - $\text{UO}_3$  seen down the tetragonal  $c$ -axis (orthorhombic  $b$ -axis).  $a_1$  and  $a_2$  are the basal axes of the tetragonal cell and  $a_0$  and  $b_0$  the axial directions for the orthorhombic cell. The tetragonal  $z$ -coordinates of the atoms are shown in hundredths of  $c$ . The bridging of the U(2) octahedral chains by U(1) atoms is clear; the O(3) atoms are superposed in projection.

On inspecting a model of the  $\gamma$ - $\text{UO}_3$  structure, it is striking that the arrangement around U(1) is essentially distorted dodecahedral. The distortion arises from the withdrawal of two of the oxygen atoms to positions 3.045 Å distant from U(1).

A dodecahedron is formed by the corners of two mutually perpendicular trapezoids, as shown in Fig. 6, and has the characteristic angles of  $70.4^\circ$ ,  $71.3^\circ$ , and  $147.0^\circ$  (8). The angles found in  $\gamma$ - $\text{UO}_3$  (293°K) are  $70.8^\circ$ ,  $78.7^\circ$ , and  $131.9^\circ$ . Thus, the geometry in this plane is very suggestive of dodecahedral symmetry (Fig. 7). It is certainly far removed from octahedral symmetry, which would require the O(1) and O(2) atoms to form a square with U(1) in the centre, the above angles to be  $90^\circ$  and the short U(1)–O(3) bonds to be uranyl bonds normal to the square.

The plane of the U(1) atom and the four

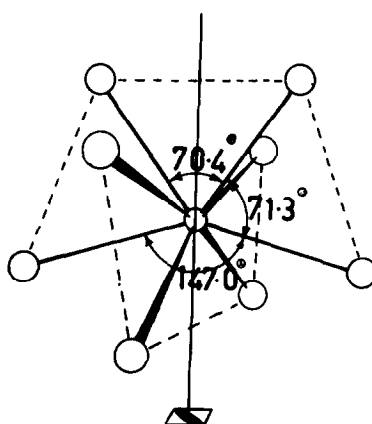


FIG. 6. The most favorable dodecahedron (8).

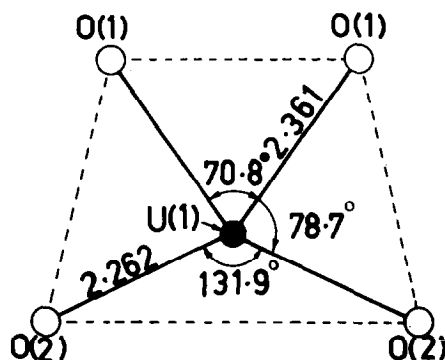


FIG. 7. The arrangement of the atoms around U(1) in the U(1), O(1), O(2) plane.

O(3) atoms is shown in Fig. 8. Here the arrangement is more distorted from dodecahedral symmetry, with U–O(3) bonds of 1.796(6) Å and 3.045(6) Å and O(3)–U–U(3) angles of  $60.0^\circ$ ,  $66.2^\circ$ , and  $173.9^\circ$ . The overall bridging scheme distorts the atoms in this plane from dodecahedral. The U(1)–O(3) distance of 1.796 Å is 0.1 Å longer than the uranyl distance, and therefore this bond is not terminal. This O(3) atom forms an asymmetric bridge between U(1) atoms, the bridge distances being 1.796 Å and 3.045 Å. The observations that (i) the O(3)–U(1)–O(3) angle of  $173.9(6)^\circ$  is significantly different from  $180^\circ$ , and (ii) the short U(1)–O(3) distance is longer than the uranyl distance imply that the U(1)–O(3) interaction at 3.045 Å is significant in the U(1) coordination polyhedron, and U(1) is eight-coordinate.

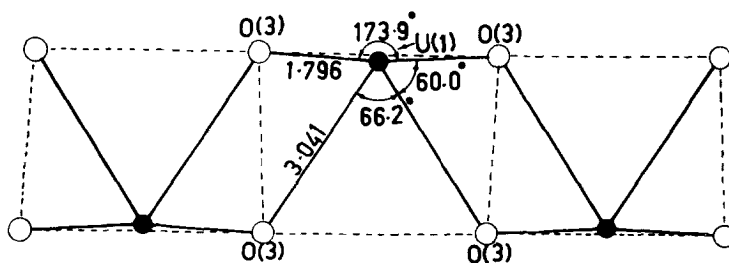


FIG. 8. The arrangement of the atoms around U(1) in the U(1), O(3) plane.

The edge-fused chains of U(2) based octahedra form the backbone of the  $\gamma$ - $\text{UO}_3$  structure, and the peculiar 8-coordinate geometry around U(1) arises from the necessity for U(1) to bridge the former chains in the  $a_1$  and  $c$  directions. The configuration around U(1) is perhaps best described as dodecahedral with two ligands partially withdrawn (dodecahedral - 2), or alternatively (octahedral + 2).

The neutron diffraction results, which show no pure uranyl bonding, are in agreement with the previous infrared data.

#### (c) Influence of Temperature on the $\gamma$ - $\text{UO}_3$ Structure

As mentioned above,  $\gamma$ - $\text{UO}_3$  is tetragonal above 323°K, and transforms smoothly to an orthorhombic phase, only slightly distorted from the tetragonal phase. Thus, in Table VI, we see the bond lengths and angles change very little on going from 373°K to 293°K. The phase at 293°K is so little removed from tetragonal that the R-factors are nearly as good for the pseudotetragonal refinement as those for the refinement in the real orthorhombic cell.

Just as the orthorhombic phase at 293°K will refine in the pseudotetragonal space group, we find that the lower-symmetry phase at 77°K will refine in the pseudo-orthorhombic  $F_{ada}$  space group; the distances and angles from the 77°K refinement in Table VI are probably close to the real values.

The distances and angles in the 373°K, 293°K, and 77°K refinements in Table VI indicate that the U(2) octahedron remains essentially unchanged in its interatomic distances and angles. There appears to be some changes however, in the U(1) polyhedron

dimensions. From 373°K to 77°K the short U(1)-O(3) distance contracts from 1.796(6) to 1.763(7) Å, and the O(3)-U(1)-O(3) angle goes from 174.6(5)° to 178.8(7)°. The other angles around U(1) remain much the same. Thus, on cooling, O(3) tends to become terminal and the short U(1)-O(3) distance approaches the uranyl distance. The cell dimensions in Table I show anisotropic changes on cooling, the  $a$ -axis expanding and  $b$  and  $c$  contracting. The symmetry change must be a result of relative movements of the octahedra and dodecahedra, the dimensions of the dodecahedra also changing slightly. The O(3) atoms of the U(1) polyhedron move the most. Relative rotations of octahedra occur on heating in  $\beta$ - $\text{UO}_2(\text{OH})_2$  (9, 10), and the latter compound also shows anisotropic thermal expansion behavior.

#### (d) Summary

The present neutron profile studies have provided precise positional parameters for  $\gamma$ - $\text{UO}_3$  at 373°K, 293°K, and 77°K, the latter being refined in a pseudo space group. The new parameters have enabled the true coordination polyhedra around U(1) and U(2) to be determined, and the results are in accord with the infrared spectrum at 293°K, which shows no uranyl bonding.  $\gamma$ - $\text{UO}_3$  shows three distinct phases between 373°K and 77°K—a tetragonal phase, an orthorhombic phase and a third phase of lower symmetry.

At this juncture,  $\gamma$ - $\text{UO}_3$  is crystallographically the best defined of the  $\text{UO}_3$  phases. It is also thermodynamically the most stable. The phase changes are a result of the mixed coordination-number structure, the unusually coordinated U(1) atom attempting to bridge

the normal octahedral chains in two different directions.

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