détermine la direction des rayons réfléchis au moyen du montage II. Dans ce cas, il est avantageux de maintenir la divergence du faisceau incident à sa valeur minimum (1,5') et l'on isole, à l'aide de la fente règlable F', une raie de la série (A), une raie de la série (B), ou un couple de raies (A) et (B) contigues. On trouve bien pour le doublet (B) un écart angulaire égal à deux fois la différence des angles de Bragg θ_{α_1} et θ_{α_2} et, de plus, il n'y a aucun déplacement des directions de réflexion lorsque la raie (B) se déplace d'un sillon au suivant. A chaque raie (A) correspondent également deux faisceaux réfléchis, de même écart angulaire, et respectivement parallèles aux faisceaux donnant naissance au doublet (B). Cependant ces résultats ne tiennent compte que de la partie la plus intense des réflexions données par les sillons. En réalité, en observant plus précisément ces images (Fig. 10), on constate que les raies intenses $K\alpha_1 K\alpha_2$ correspondant au paramètre unique sont entourées de part et d'autre d'une bande de noircissement assez faible qui est limitée par deux renforcements. Cette bande extérieure est particulièrement intense aux points qui correspondent aux croisées des sillons. Étant donné que le faisceau incident a une direction bien déterminée, une variation de la direction du rayon réfléchi ne peut provenir que d'une variation de l'angle de Bragg, donc d'une variation du paramètre du cristal réfléchissant. Les observations s'interprètent donc en admettant que, dans les sillons, il y a, en plus du cristal à paramètre unique qui forme la partie principale, une petite quantité de cristallites dont la distance réticulaire peut varier entre les deux limites d_1 et d_2 des cristaux plus simples étudiés précédemment. Ces cristallites seraient particulièrement nombreux à la croisée de deux sillons. En outre, pour que ces cristallites à paramètres variables puissent réfléchir les rayons incidents d'orientation bien précise, il faut qu'ils aient des orientations variées, ce serait donc des grains un peu désorientés et de structure un peu différente de celle du cristal parfait.

Ces quelques exemples montrent la richesse des possibilités de la méthode de Berg–Barrett. Indépendamment de l'image classique qui permet d'obtenir une carte des imperfections ou des désorientations du cristal, on peut, en variant les conditions d'utilisation du montage: angle d'ouverture du faisceau incident, distance du film à l'échantillon, dimensions de la surface explorée, faire une étude locale précise du cristal. Nous avons montré que l'on pouvait ainsi déterminer des désorientations avec une précision de l'ordre de la minute, et apprécier des variations relatives locales de paramètre de 10^{-3}. En améliorant l'appareillage ces mesures pourraient être faites pour des domaines n'ayant pas plus de 1/100e mm, leur position étant repérée avec la même précision. Un tel pouvoir de résolution nous permettrait d'interpréter les photographies de certains cristaux de structure complexe analogues à ceux décrits précédemment et qui donnent des raies (A) et (B) non pas continues mais ponctuées; la Fig. 11 représente alors une image de la surface, obtenue en ouvrant la fente F de façon que toute la surface puisse réfléchir. Les stries fines observées ont une dimension moyenne de 1/100e mm, l'origine du contraste n'a pu être déterminée jusqu'à présent.

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The Crystal Structure of γ-UO_3

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The structure of γ-UO_3 has been determined from powder diffraction data, integrated diffractometer intensities being used. The structure is regarded as tetragonal with $a = 6{\cdot}89$ Å, $c = 19{\cdot}94$ Å, though actually $\gamma = 90{\cdot}34°$. Uranium is found to occur in two 8-fold positions of the space group $I4_1/amd$, both in octahedral coordination. Of the three 16-fold oxygen positions, one is found to have only one uranium neighbour.

1. Introduction

γ-UO_3 is one of the six known modifications of this oxide (Hoekstra & Siegel, 1958). Its published powder diffraction pattern (*e.g.* Connolly, 1959) has been indexed (de Wolff, 1961) on the basis of a pseudo-tetragonal unit cell, with extinctions strongly indicating that the structure to which it approximates has

Table 1. *Powder diffraction data*

Q_o	Q_c	hkl	I
235	236	101	5
402	402	004	29
436	437	103	3
522	519	$1\bar{1}2$	44
	524	112	
841	839	105	100
	842	200	
943	942	202	43
1079	1072	$2\bar{1}1$	36
	1082	211	
1281	1274	$2\bar{1}3$	60
	1284	213	
1326	1323	$1\bar{1}6$	10
	1328	116	
1442	1442	107	11
1683	1674	$2\bar{2}0$	
	1693	220	2
	1676	$2\bar{1}5$	
	1711	215	
1746	1746	206	7
1918	1919	301	1
2075	2076	$2\bar{2}4$	15
2094	2096	224	
2121	2121	303	4
2203	2197	$3\bar{1}2$	10
	2212	312	
2246	2247	109	13
2287	2279	$2\bar{1}7$	1
	2289	217	
2451	2451	208	9
2522	2522	305	12
2746	2746	$3\bar{2}1$	9
2775	2776	321	
2947	2932	$1,\bar{1},10$	
	2937	1,1,10	22
	2947	$3\bar{2}3$	
2977	2976	323	
3014	3002	$3\bar{1}6$	11
	3017	316	
3127	3126	307	2
3251	3252	1,0,11	7
3294	3282	$2\bar{2}8$	25
	3302	228	
3369	3367	400	
	3356	2,0,10	22
	3349	$3\bar{2}5$	
	3379	325	
3608	3620	0,0,12	
	3593	$4\bar{1}1$	4
	3612	411	
3772	3769	404	
	3765	$3\bar{3}0$	5
	3810	330	
3938	3930	309	3

the space group $I4_1/amd$. This high degree of symmetry induced us to attempt to solve the structure from the powder pattern.

2. The powder diffraction pattern

A sample of γ-UO_3 was kindly prepared for us by Ir. M. E. A. Hermans (KEMA, Arnhem). It is a bright-yellow powder obtained by ignition of $UO_2(NO_3)_2 . 6H_2O$ in air at temperatures between 400 and 600 °C.

The X-ray diffraction pattern of this sample was substantially identical with published patterns. The lines were slightly broadened; several doublets in Connolly's data appear unresolved in our pattern. On the other hand, six unindexable lines among Conollys results were now absent. The width of the lines varied somewhat with the indices in such a way as to indicate platy crystals with a dimension of about 400 Å in the c direction and 500 Å in the a and b directions. The powder diffraction data are listed in Table 1. Unit-cell dimensions have been determined by the method of least squares with the result

$$a=b=6{\cdot}89 \text{ Å},\ c=19{\cdot}94 \text{ Å};\ \alpha=\beta=90°,\ \gamma=90{\cdot}34°$$

($Z=16$) as compared with

$$a=b=6{\cdot}91 \text{ Å},\ c=19{\cdot}91 \text{ Å};\ \gamma=90{\cdot}57°$$

for the pattern published by Connolly.

We think the difference both in c/a and in γ is significant. It may be related to a difference in purity which, however, has in neither case been investigated.

3. Structure determination

Integrated intensities have been obtained originally from photometer recordings of Guinier photographs. After conversion to F^2 values by a crude Lorentz-polarization correction, these data were used to find the coordinates of uranium atoms. The 16-fold positions in the space-group $I4_1/amd$ led to contradictions because they require the unobserved 008 to be stronger than 228. Fair agreement was obtained by placing 8U in position (e) with $z=0{\cdot}060$, and 8U in position (d). This yielded a value of the reliability index $R=\Sigma|F_o-F_c|/\Sigma|F_o|$ of 14%. However, the discrepancies for some reflexions still seemed very large.

At this stage it was discovered that the ratio F_o/F_c did show a strong correlation with the angle between the reflecting plane and the c axis. New measurements of both Guinier and diffractometer records of differently prepared samples soon confirmed that the original data suffered from preferred orientation. The ratio of $00l-$ to $hk0$ intensities was estimated to be in error by as much as a factor of 2. For the final stage of the analysis, diffractometer integrated intensities (Cu $K\alpha$ radiation) were used, obtained from a sample which had been mixed with Canada balsam and then reground after drying. It is believed that the error in the above-mentioned ratio is now at most 10%. The resulting values of F_o, corrected by the well-established Lorentz-polarization factor for diffractometer work, are shown in Table 2. For the purpose of structure determination, the crystal is considered to be tetragonal. So the intensities of

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c
101	104	−142·3
004	672	+697·5
103	113	+ 98·8
112	467	−446·3
105, 200	741	679·0
202	633	+608·9
211	437	+470·3
204	< 80	+ 32·6
213	624	−617·9
116	377	−413·6
107	413	−392·8
008	<160	− 8·7
220, 215	110	108·4
206	350	+359·0
301	120	−126·7
224	588	+515·4
303	210	+201·4
312	352	−363·4
109	573	−553·5
217	160	−159·6
208	494	−518·3
305	585	−591·4
321	380	−387·8
1,1,10, 323	500	543·0
316	443	−401·2
307	296	−340·9
1,0,11	534	−573·4
228	994	+953·4
402	<140	+ 8·4

Table 3. *Atomic coordinates*

			y	z
U(2)	(*d*)	(0, 0, 0; ½, ½, ½)+0, 0, ½; 0, ½, ½; ¼, ¼, ¼; ¼, ¾, ¾	0	0
U(1)	(*e*)	(0, 0, 0; ½, ½, ½)+0, ¼, *z*; 0, ¾, ¼+*z*; 0, ¾, $\bar{z}$; 0, ¼, ¾−*z*	¼	0·060
O(1)	(*h*)	(0, 0, 0; ½, ½, ½)+0, *x*, *z*; 0, ½−*x*, *z*; ¼+*x*, ¼, ¾+*z*; ¾−*x*, ¼, ¾+*z*; 0, $\bar{x}$, $\bar{z}$; 0, ½+*x*, $\bar{z}$; ¾−*x*, ¾, ¼−*z*; ¼+*x*, ¾, ¼−*z*	0·547	0·070
O(2)	(*h*)		0·943	0·406
O(3)	(*h*)		0·039	0·264

hkl, $-hkl$ doublets have been added to give the *hkl* intensity, whether the doublet is resolved or not. For three other unresolved doublets, an average F_o has been listed, calculated from the integrated intensity and a multiplicity factor equal to the sum of the factors of both reflexions.

The positions of the oxygen atoms had been established in the former stage from a difference synthesis projected along [100] (assuming all signs to be determined by the uranium contributions), together with space-filling considerations. In the present stage, these positions were confirmed in a completely direct manner by a difference Fourier section in the plane $x=0$. The six reflexions forming the unresolved doublets were left out from this synthesis. Fig. 1 shows that all the oxygen atoms are clearly brought out. They occupy three 16-fold positions (*h*).

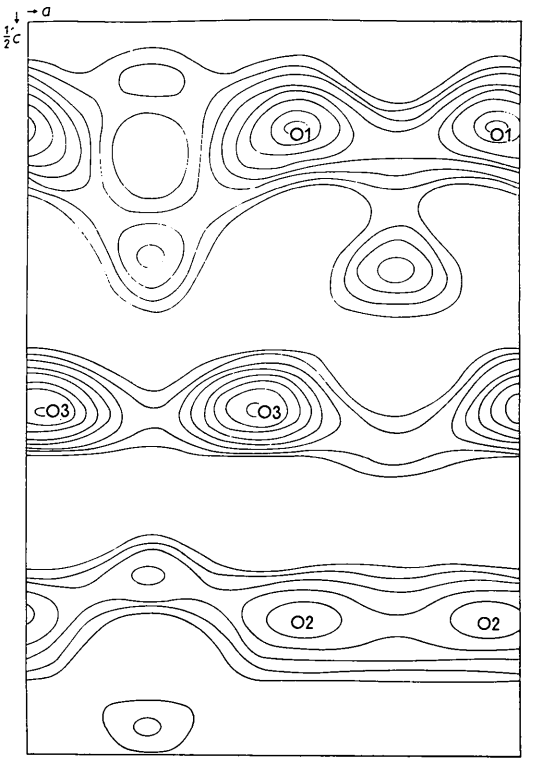

Fig. 1. (F_o-F_c) Difference Fourier section $x=0$, F_c from uranium contribution only. This section shows high maxima for the O(1), O(2) and O(3) atoms lying in the plane $x=0$ and lower peaks (not marked) for other oxygen atoms (*cf.* Fig. 2).

For the final calculated structure factors F_c listed in Table 2, the reliability factor (not counting the three unobserved reflexions) is $R=6{\cdot}0\%$. A temperature factor with $B=1{\cdot}5$ Å^2 had been derived by the method of least squares. The optimum value for the uranium *z* coordinate has been determined by calculating *R* for a number of *z* values at intervals of 0·0025. The oxygen coordinates have been taken as the peak positions in the difference synthesis at $x=0$.

4. Description of the structure

All uranium atoms are surrounded by somewhat distorted octahedra of oxygen atoms. The octahedra surrounding U(2) share edges, thus forming strings which run in the *a* and *b* directions at different *z* levels (*cf.* Fig. 2). These strings are not immediately connected, but each octahedron surrounding U(1) shares corners with strings in both directions. The O(1)-atoms of the latter octahedra have only one

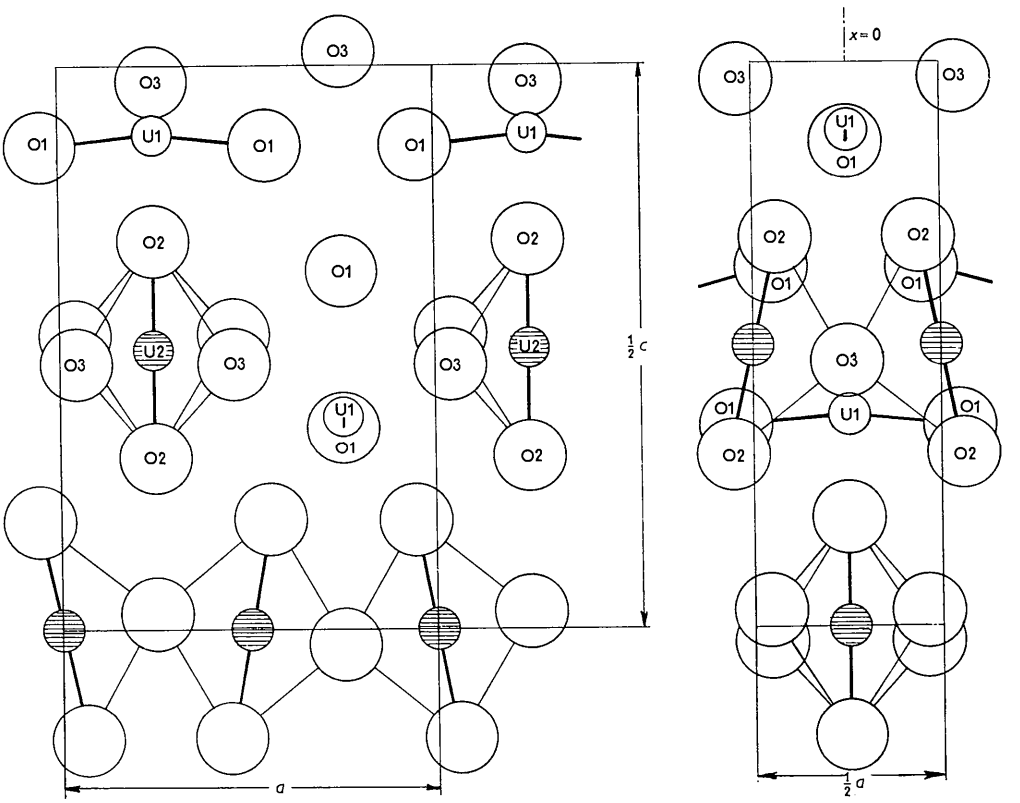

Fig. 2. Projections along [100] and along [010] of a part of the structure of γ-UO_3. The octahedral environment of U(2) is indicated. The two O(1)-atoms with bonds to U(1) only are drawn as UO_2 groups, though here also an octahedron is formed. The portion indicated by *a* corresponds to Fig. 1.

(U(1)) metal neighbour, whereas O(2) has two and O(3) has three such neighbours. The bonding distances are shown in Table 4. We estimate the r.m.s. error in the U-positions to be 0·03 Å and those in the oxygen positions 0·1 Å. Therefore the bond distances do not give a clear indication of the bond character. In view of the coordination, however, U(1)+2O(1) can be called a uranyl ion and the chemical formula could accordingly be written as $(UO_2)UO_4$, uranyl uranate.

Table 4. *Interatomic distances*

U(1)–U(2)	4·04 Å	U(2)–O(3)	2·27 Å
U(1)–U(1)	4·20	O(1)–O(1)	2·79
U(2)–U(2)	3·45	O(1)–O(2)	2·97
U(1)–O(1)	2·06	O(1)–O(3)	3·05
U(1)–O(2)	2·34	O(2)–O(2)	3·24
U(1)–O(3)	2·19	O(2)–O(3)	2·92
U(2)–O(1)	3·60	O(3)–O(3)	2·91
U(2)–O(2)	1·91		

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