The Crystal Structure of the High Temperature Modification of U_3O_8

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The crystal structure of the high-temperature form of U_3O_8 (known as 'hexagonal U_3O_8') was re-investigated by a combination of X-ray and neutron powder techniques. It was found that the structure is pseudohexagonal (strictly speaking orthorhombic) space group *Amm2*. Two of the uranium atoms are bonded to six oxygen atoms forming the corners of a distorted octahedron; the other four uranium atoms are surrounded by seven oxygen atoms, which form an irregular pentagonal bipyramid. All the uranium atoms belong to continuous –O–U–O– chains lying along the *a* axis.

Introduction

The crystal structure of the high-temperature modification of U_3O_8 was first determined by Siegel (1955) from X-ray powder data. Siegel's model was based on the trigonal space group $P\bar{3}$, and on a unit-cell of dimensions: $a=6\cdot815$, $c=4\cdot136$ Å; it was derived from the structure of the room-temperature orthorhombic modification of U_3O_8 (α-U_3O_8), solved by Zachariasen (1945, 1948) from X-ray powder data. However, the structure of α-U_3O_8 was subsequently considerably modified when the X-ray single-crystal data (Chodura & Malý, 1958) and neutron powder data (Andresen, 1958, Loopstra, 1964) became available. Hence, it is conceivable that the proposed structure for the high temperature form of U_3O_8 may also need modification.

In the present work the structure of the latter phase of U_3O_8 has been reinvestigated by a combination of X-ray and neutron powder techniques.

Experimental

The X-ray and neutron diffraction data were collected from powder samples of U_3O_8 of nuclear purity, ob-tained by calcination of ammonium diuranate at 750 °C. For X-ray data, an MRC high temperature camera and a Philips PW 1010 generator were used. The intensities were recorded with a proportional counter in conjunction with a pulse height analyser; Ni–filtered Cu radiation was used. The neutron data were collected with a MAN diffractometer at the RA nuclear reactor at Vinča. The U_3O_8 powder was placed in an aluminum holder with dimensions $20 \times 40 \times 7$ mm and a wall thickness of $0\cdot1$ mm which was mounted on a specially designed high temperature attachment. A monochromatic neutron beam, with $\lambda = 1\cdot066$ Å, obtained by diffraction of neutrons from the (111) plane of a Cu monocrystal, was used. No absorption correction to the measured intensities was necessary. The powder diagrams, both X-ray and neutron (Figs. 1 and 2) were recorded at 500 °C in air.

The O/U ratios of samples before and after heating at 500 °C, determined by the polarographic method (Branica & Scipos, 19. .), were found to be almost identical, which indicated that no significant change in the oxygen content had occurred during heating. An independent check by thermogravimetric analysis with the use of a Stanton microbalance also showed that
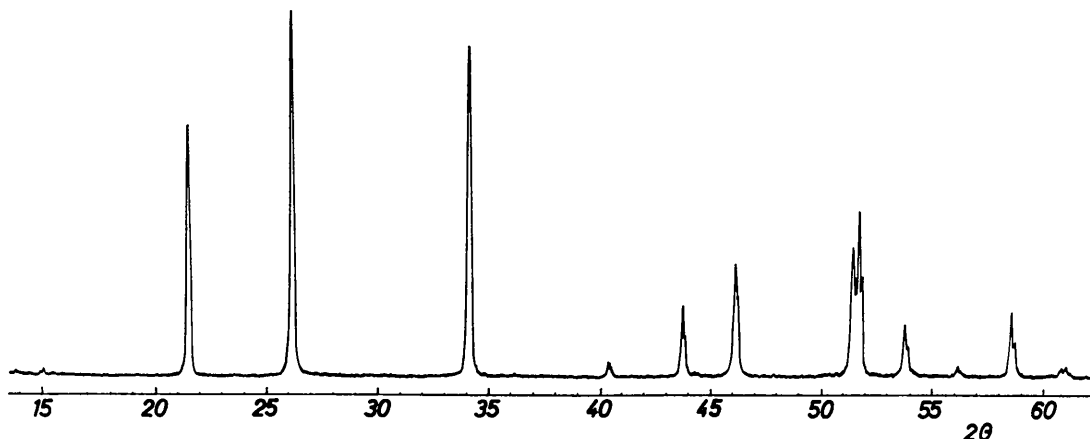

Fig. 1. X-ray powder diagram of the high temperature form of U_3O_8 (at 500 °C).

the weight of the samples was not changed by heating.

Determination of the structure

Both X-ray and neutron powder diagrams of the high-temperature form of U_3O_8 can be indexed on the basis of the hexagonal cell. However, an important feature of the neutron diagram is that it closely resembles the neutron diagram of α-U_3O_8, which is known to have orthorhombic symmetry and five oxygen atoms around the uranium atom in the $x=0$ plane (Loopstra, 1964). Furthermore, a few weak lines are observed on the X-ray diagram for which the uranium contribution should be zero if the uranium atoms are in the positions $(0,0,0)$,

Table 1. *The neutron powder data. Calculated (I_c) and observed (I_o) intensities*

ΣI_c is the sum of I_c for the overlapping reflexions.

h	k	l	I_c	ΣI_c	I_o		h	k	l	I_c	ΣI_c	I_o
0	2	0	56	76	67		0	9	1	12		
0	1	1	20				1	1	5	58		
1	0	0	1624	1624	1552		0	6	4	358		
0	3	1	1267				0	3	5	99		
1	2	0	2	2051	1966		1	8	2	29		
1	1	1	1				1	7	3	157	1063	970
0	0	2	781				2	7	1	173		
0	4	0	7	57	0		2	2	4	4		
0	2	2	50				2	5	3	57		
1	3	1	59	73	55		3	3	1	6		
1	0	2	14				3	0	2	1		
1	4	0	103	242	348		3	2	2	31	53	52
1	2	2	139				3	4	0	22		
0	5	1	207				1	9	1	11		
0	4	2	613	972	1035		1	6	4	77	159	148
0	1	3	152				1	3	5	71		
2	0	0	1436	1436	1604		2	8	0	1	65	40
0	6	0	906				2	4	4	64		
1	5	1	103				0	5	5	34		
1	4	2	453				0	10	0	11		
2	2	0	11	3387	3408		3	1	3	87	302	348
2	1	1	4				3	4	2	139		
0	3	3	1620				3	5	1	31		
1	1	3	290				0	0	6	249		
1	6	0	352				0	9	3	207		
1	3	3	452	1852	2302		1	10	0	10		
2	3	1	650				1	5	5	16		
2	0	2	398				2	1	5	56		
0	6	2	374				2	7	3	15		
0	0	4	414	822	670		2	8	2	86	1259	1062
2	2	2	30				3	3	3	170		
2	4	0	4				3	6	0	127		
0	7	1	148				0	2	6	15		
0	5	3	49	201	186		0	8	4	12		
0	2	4	4				0	10	2	296		
1	6	2	1	63	87		1	9	3	46		
1	0	4	62				1	0	6	89		
1	2	4	7				2	6	4	490		
1	7	1	23				2	3	5	138		
1	5	3	12	826	795		2	9	1	166	1116	1068
2	1	3	127				1	2	6	16		
2	5	1	166				1	8	4	1		
2	4	2	490				1	10	2	170		
0	8	0	1	52	24		3	0	4	28		
0	4	4	51				3	6	2	2		
2	6	0	888	2480	2376		0	7	5	168		
2	3	3	1592				0	4	6	1		
1	4	4	28				0	11	0	86	304	321
1	8	0	39	228	289		3	2	4	3		
3	0	0	160				3	5	3	5		
0	1	5	43				3	7	9	11		
0	8	2	65				4	0	0	291		
0	7	3	13	121	139		2	10	0	18		
3	1	1	0				2	5	5	49		
3	2	0	0				1	11	1	53	550	504
2	6	2	425	889	839		1	4	6	19		
2	0	4	464				1	7	5	116		
							4	1	1	1		
							4	2	0	3		

$(\frac{1}{2},\frac{2}{3},0)$ and $(\frac{2}{3},\frac{1}{3},0)$ in a hexagonal cell, as proposed by Siegel. Siegel's trigonal model is therefore ruled out. A new orthorhombic cell was introduced, with $a = 4\cdot136 \pm 3$, $b = c \sqrt{3} = 11\cdot816 \pm 7$ and $c = 6\cdot822 \pm 4$ Å, and with two U_3O_8 formula units per unit cell. Systematic absences of reflexions eleminated the orthorhombic space groups $A222$, $A2mm$, $Amm2$ and $Ammm$ as possible ones.

According to the neutron diagrams there is some important similarity between the structure of the α-U_3O_8 and the high-temperature modification, therefore space group $Amm2$, the same as for α-U_3O_8 (Loopstra, 1964) was chosen.

The positions of the uranium atoms were determined from X-ray data. The uranium atoms were placed as: $2U(1)$ in $a(0,0,z)$ and $4U(2)$ in $d(0,y,z)$. Structure factors were then calculated including only the contributions of the uranium atoms for a number of different parameter values, and the positions $(0,0,0)$ and $(0, 0\cdot318,0)$, values which gave the best agreement of calculated and observed intensities, were chosen as the final ones.

The positions of the oxygen atoms were determined from neutron data. It was assumed that–O–U–O chains, lying along the a axis in the α-U_3O_8 structure, also exist in the high-temperature form; with the positions of the uranium atoms already determined from X-ray data, there remained only five parameters to be determined. By a trial and error procudure, based on comparison of observed and calculated intensities, the best parameters for the oxygen atoms were collected. At the last stage of refinement two isotropic thermal parameters, B, one for all the uranium and one for all the oxygen atoms, were introduced. Their final values were: $B_U = 1\cdot0$ and $B_O = 1\cdot4$ Å^2.

The final agreement index, of the form

$$R = \underset{u}{\Sigma} \underset{g}{\Sigma} |I_{obs} - I_{calc}| / \underset{u}{\Sigma} \underset{g}{\Sigma} I_{obs}$$

($\underset{u}{\Sigma}$ is the sum over all peaks which can be separated in the diagram, $\underset{g}{\Sigma}$ is the sum over the overlapping re-

flexions in one peak) is $8\cdot8\%$. This value should be compared with $R = 44\%$, which is obtained for the neutron powder data if the I_{calc} are based on Siegel's structure. The final list of observed and calculated values of intensities is given in Table 1.

Because of the heavy overlapping of many reflexions in both powder diagrams, and because of the refinement procedure which was limited by our computing facilities, further refinement could not be expected to lead to a more reliable structure. The final fractional parameters are presented in Table 2 and the interatomic distances in Table 3. In Fig. 3 the new model of the crystal structure of the high-temperature form of U_3O_8 is compared with that proposed by Siegel.

Table 2. *Final fractional coordinates*

	x	y	z
U(1)	0	0	0
U(2)	0	0·318	0
O(1)	0·500	0	0
O(2)	0·500	0·318	0
O(3)	0	0	0·540
O(4)	0	0·140	0·194
O(5)	0	0·347	0·315

Table 3. *Interatomic distances* (Å)

U(1)–O(1)	2·07	U(2)—O(5″)	2·18
U(1)–O(3″)	3·14	O(3′)–O(4′)	2·88
U(1)–O(4′)	2·12	O(3′)–O(5″)	2·60
U(1)–O(5′)	2·20	O(5″)–O(4″)	2·58
U(2)–O(2)	2·07	O(4″)–O(5′)	2·59
U(2)–O(3′)	2·17	O(5′)–O(4′)	2·58
U(2)–O(4′)	2·14	O(5′)–O(3″)	2·60
U(2)–O(4″)	2·48	O(4″)–O(4‴)	3·31
U(2)–O(5′)	2·32		

There are some indications that the transition of α-U_3O_8 to the high-temperature form is a second-order phase transformation. The theory of Landau & Lifshitz (1958) requires that the symmetry of the two modifications be related, *i.e.* the point group of one modification is a sub- or super-group of the other; the super-group for $Amm2$, with the same systematic ab-
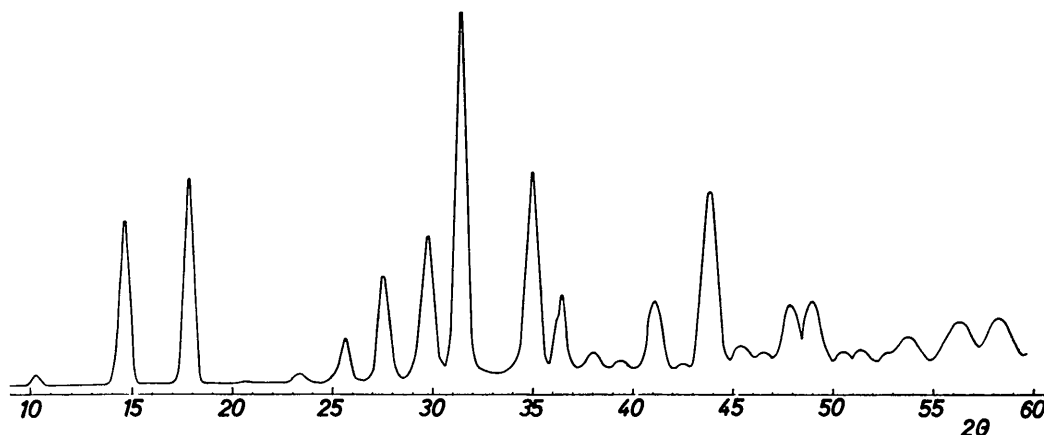

Fig. 2. Neutron powder diagram of U_3O_8 at $500°C$ (the instrumental background is subtracted).

sences, is *Ammm*. The calculation of the intensities with the oxygen atoms in some positions of the *Ammm* group led to a higher value of the *R* index than the minimum obtained (8·8%).

Computation of structure factors was done on a ZUSE Z23 machine. In this procedure the X-ray scattering factor used for uranium was $(2f_U6+ +f_U4+)/3$ with f values computed by Cromer & Waber (1965). The neutron scattering lengths were taken to be $0·85 \times 10^{-12}$ cm for uranium and $0·577 \times 10^{-12}$ for oxygen.

Discussion

As can be seen from Fig.3, uranium U(2) atoms are surrounded by seven oxygen atoms, which form irregular pentagonal bipyramids; each uranium U(1) atom is bonded to six oxygen atoms which form the corners of a distorted octahedron. As was expected, this model of the structure of the high-temperature form differs from that proposed by Siegel in the same manner as Loopstra's model for α-U_3O_8 from Zachariasen's. The value obtained for the *R* index may be considered as a confirmation that all the uranium atoms (not just $\frac{2}{3}$ of them as in Siegel's model) belong to continuous –O–U–O– chains along the *a* axis.

Different coordinations for uranium atoms were also found in β-UO_3 (Debets, 1966), γ-UO_3 (Engman & de Wolf, 1963) and orthorhombic U_3O_8 (Loopstra, 1964).

The observed uranium–oxygen bond lengths, ranging from 2·07 to 2·48 Å, lie within the limits of those found in uranium oxides. All oxygen–oxygen distances are normal, the smallest (2·58 Å) being not far from those observed in uranium oxides: 2·55 Å, Loopstra (1964); 2·52 Å, Siegel, Hoekstra & Sherry (1966); 2·21 Å, Debets (1966).

On the basis of the bond strength–bond length curve published by Zachariasen & Plettinger (1959), the bond strengths for all U–O distances were determined. The total bond strengths for U(1) and U(2) are 5·50 and 5·65 respectively. The procedure of Vdovenko, Mashirov & Suglobov (1966) for the calculation of the bond strength was also used; values of 5·42 for U(1) and 5·49 for U(2) were obtained. The accuracy of parameters, however, is not sufficiently high to establish whether the equality of oxidation states for all the uranium atoms is obtained by chance, or whether it has some importance in the behaviour of the structure.

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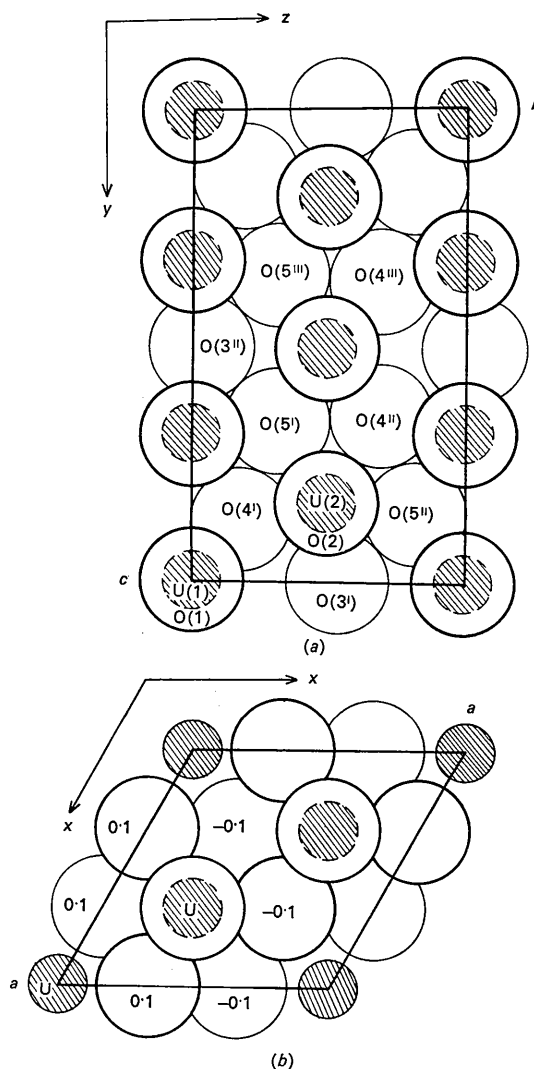

Fig.3. (*a*) The crystal structure of the high temperature form of U_3O_8 viewed along the *a* axis. The atom symbols refer to Table 3. (*b*) The crystal structure of the same form of U_3O_8 as proposed by Siegel. Numbers indicate the *z* parameters of the oxygen atoms.

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