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Refinement of the structure of β-U_4O_9

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β-U_4O_9 is a superlattice structure based on the fluorite arrangement of UO_2. The U atoms occupy positions close to those in UO_2 and the additional O atoms are accommodated in cuboctahedral clusters of $\bar{4}3m$ symmetry, which are centred on the special 12-fold sites of the cubic space group $I\bar{4}3d$. The structure has been refined from single-crystal neutron data in accordance with the procedure described in the previous paper [Popa & Willis (2004). *Acta Cryst.* A**60**, 318–321].

1. Introduction

The structure of β-U_4O_9 was described by Bevan *et al.* (1986) as an anion-excess fluorite-related oxide phase, with the excess anions accommodated in cuboctahedral clusters centred on the 12-fold sites of the cubic space group $I\bar{4}3d$. In this paper, we shall refine the same neutron data set measured at 503 K, together with an additional data set measured at 773 K, taking into account the fact that the reflection conditions of the special positions 12(b) are obeyed by all the atoms, even though most of them occupy general 48(e) sites.

Between room temperature and 1273 K, there are three phases of U_4O_9 (known as α, β, γ), all having structures based on the fluorite arrangement of UO_2. We shall be concerned with the β phase only, stable from 353 to 873 K. β-U_4O_9 is a cubic superstructure with a cell edge four times that of UO_2. It gives rise to strong fundamental reflections from the underlying fluorite framework and to very many weak superlattice reflections. The fundamental reflections reveal the contents of the 'average cell' of edge a_0, which is obtained by superimposing the 64 subcells in the $4a_0 \times 4a_0 \times 4a_0$ supercell. The superlattice reflections give the contents of the cubic supercell. We shall describe first the analysis of the fundamental intensities at 503 K.

2. Fundamental reflections: contents of 'average cell' at 503 K

According to Lauriat *et al.* (1989), the space group of the 'average cell' is $F\bar{4}3m$, and the atoms occupy the Wyckoff sites shown in Table 1. The table gives results obtained by the least-squares refinement of this model against 34 fundamental intensities, using the *CRYSTALS* program (Betteridge *et al.*, 2003).

Table 1
Average cell at 503 K; space group $F\bar{4}3m$; a_0 = 5.450 (2) Å; R = 1.9%.

	Site	x	y	z	Occupancy	Total number	$U_{\rm iso}$ (Å^2)
U	4(a)	0	0	0	1.0	4	0.0086 (2)
O	4(c)	0.25	0.25	0.25	0.87 (1)	6.9 (1)	0.0200 (4)
O	4(d)	0.75	0.75	0.75			
O′	48(h)	$x = y = 0.617$ (2)		0.5	0.038 (2)	1.8 (1)	
O″	16(e)	$x = y = z = 0.608$ (14)			0.010 (5)	0.16 (8)	

The U atoms and most of the O atoms are located at fluorite-type positions. Although there are no vacancies in the sites occupied by the U atoms within the fluorite framework, a significant proportion of the O-atom positions in this framework is unoccupied. There are two other positions available to the O atoms: O′ atoms in 48(h) (x, x, z) and O″ atoms in 16(e) (x, x, x). The O′ atoms are displaced along the $\langle 110 \rangle$ directions from the 4(b) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site, which is the centre of the large interstice in the fluorite structure, and the O″ atoms are displaced along the $\langle 111 \rangle$ directions from the same site. The refinement was restrained in order to ensure that the overall composition (see the final column in Table 1) was close to the theoretical composition of U_4O_9. The column $U_{\rm iso}$ in Table 1 gives the mean-square displacements of the U and O atoms from their xyz sites: these displacements will be discussed further in §3.5.

The results given in Table 1 are very similar to those obtained on hyperstoichiometric $UO_{2.11}$ and $UO_{2.13}$ (Murray & Willis, 1990). In UO_{2+x}, the additional O atoms are incorporated in a solid solution without the formation of a superlattice; they are displaced along $\langle 110 \rangle$ and $\langle 111 \rangle$ from the large interstices, just as in U_4O_9, but with fewer anion vacancies in the fluorite framework.

3. Fundamental and superlattice reflections: contents of 'supercell' at 503 K

The 'idealized' structure of β-U_4O_9, as proposed by Bevan *et al.* (1986), is given in Table 2, where the labels of the atoms are the same as those used in Table III of Bevan's paper.

The atoms U1–U7 occupy all the U-atom fluorite sites of UO_2, and the atoms O4–O13 occupy a fraction, 416/512, of the O-atom fluorite sites. The atoms O1, O2, O3 consist of

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Table 2
Positional parameters in idealized structure of U_4O_9; space group $I\bar{4}3d$.

Atom	Site	x	y	z	Atomic groups
U1	16(*c*)	0	0	0	256 U atoms in fluorite sites
U2	24(*d*)	1/4	0	1/4	
U3	48(*e*)	1/8	1/8	1/4	
U4	24(*d*)	0	0	1/4	
U5	48(*e*)	7/8	0	1/8	
U6	48(*e*)	0	1/8	3/8	
U7	48(*e*)	0	1/8	1/8	
O1	48(*e*)	$7/16+\delta$	$1/16+\delta$	1/4	144 O atoms in 12 cuboctahedral clusters
O2	48(*e*)	$7/16+\delta$	0	$5/16+\delta$	
O3	48(*e*)	7/8	$1/16+\delta$	$5/16+\delta$	
O4	16(*c*)	1/16	1/16	1/16	416 O atoms in fluorite sites
O5	16(*c*)	3/16	3/16	3/16	
O6	48(*e*)	1/16	3/16	3/16	
O7	48(*e*)	1/16	1/16	3/16	
O8	48(*e*)	7/16	1/16	1/16	
O9	48(*e*)	7/16	1/16	7/16	
O10	48(*e*)	7/16	3/16	3/16	
O11	48(*e*)	7/16	3/16	5/16	
O12	48(*e*)	1/16	1/16	5/16	
O13	48(*e*)	7/16	3/16	7/16	
O14	12(*b*)	7/8	0	1/4	12 O atoms in cluster centres

Table 3
Constrained model adhering to the 12(*b*) special reflection conditions for space-group-type $I\bar{4}3d$.

Variable positional parameters are a_1–a_4 and b_1–b_8.

Atom	Site	x	y	z	Atomic groups
U1	16(*c*)	0	0	0	
U2	24(*d*)	$1/4+a_1$	0	1/4	Octahedron 72 atoms
U3	48(*e*)	1/8	$1/8-a_1$	1/4	
U4	24(*d*)	a_2	0	1/4	Octahedron 72 atoms
U5	48(*e*)	7/8	0	$1/8-a_2$	
U6	48(*e*)	$-a_3$	$1/8-a_3$	$3/8-a_3$	Tetrahedron 48 atoms
U7	48(*e*)	$-a_4$	$1/8-a_4$	$1/8+a_4$	Tetrahedron 48 atoms
O1	48(*e*)	$7/8+b_1$	b_1	$1/4+b_2$	Skewed cuboctahedron 144 atoms
O2	48(*e*)	$7/8+b_1$	b_2	$1/4+b_1$	
O3	48(*e*)	$7/8+b_2$	b_1	$1/4+b_1$	
O4	16(*c*)	1/16	1/16	1/16	
O5	16(*c*)	3/16	3/16	3/16	
O6	48(*e*)	$1/16-b_3$	$3/16-b_3$	$3/16+b_3$	
O7	48(*e*)	$1/16+b_4$	$1/16+b_5$	$3/16-b_5$	Hexatetrahedron 288 atoms
O8	48(*e*)	$15/16+b_5$	$1/16+b_5$	$1/16-b_4$	
O9	48(*e*)	$15/16-b_6$	$1/16-b_6$	$7/16+b_4$	
O10	48(*e*)	$15/16+b_5$	$3/16+b_4$	$3/16-b_5$	
O11	48(*e*)	$15/16-b_6$	$3/16+b_4$	$5/16-b_6$	
O12	48(*e*)	$1/16+b_4$	$1/16-b_6$	$5/16-b_6$	
O13	48(*e*)	$15/16-b_7$	$3/16-b_7$	$7/16+b_7$	
Empty	12(*b*)	7/8	0	1/4	Cluster centre
O15	48(*e*)	$7/8+b_8$	b_8	$1/4+b_8$	Tetrahedron 12 atoms

twelve 12-atom clusters with cuboctahedral symmetry (see Fig. 1), which are centred on the 12(*b*) positions of the $I\bar{4}3d$ space group. The size of the clusters is determined by the magnitude of the parameter δ in Table 2, which was the only significant parameter determined by Bevan *et al.* The atoms O14 occupy the centres of these clusters.

Using the idealized model inTable 2 as a starting point, parameters were refined against the intensities of 34 fundamental and 387 superlattice reflections using the *CRYSTALS* program. To adhere to the 12(*b*) special extinction conditions of $I\bar{4}3d$, it was necessary to constrain the model so that pure translation operations exist between the clusters at each of the sites as described in paper I (Popa & Willis, 2004). The $\bar{4}$ axes of the 12(*b*) sites are variously orientated so that four are parallel to each unit-cell axis and as a result the additional translational symmetry constraints demand that each cluster has $\bar{4}3m$ symmetry. These constraints are listed in Table 3. In all, there are four positional variables (a_1–a_4) for the U atoms and eight (b_1–b_8) for the O atoms. Table 4 gives the final list of these 12 parameters. Structure-factor calculations for this final model gave exactly zero intensity for the reflections forbidden by the 12(*b*) rules.

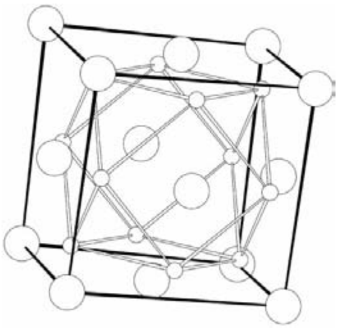

Figure 1
A schematic diagram of the Bevan cuboctahedral cluster. The 12 anions in the cluster are shown as small circles, and the surrounding cations (in fluorite-type sites) as larger circles. The anions are displaced along the 12 ⟨110⟩ directions from the centre of the cluster.

The centre of the cluster at O14 is unoccupied, and the O atom that occupies the centre in the Bevan model is displaced along [111] to the O15 site. The atomic groupings in Table 3 indicate how the various sites are combined in accordance with $\bar{4}3m$ point-group symmetry.

3.1. Cuboctahedral cluster of O atoms

The centre of each cluster is surrounded by a cuboctahedral arrangement of O atoms (O1, O2 and O3 in Fig. 2). These correspond to the O′ atoms displaced along ⟨110⟩ from the 4(*b*) cation sites in the $F\bar{4}3m$ average cell (Table 1). The symmetry constraints permit two parameters to be refined. The first parameter (b_1) defines the size of the cluster. The second (b_2) determines the extent of the change from $m3m$ to $\bar{4}3m$ symmetry: thus, the four triangular faces in Fig. 2 that are normal to the tetrahedral directions ⟨111⟩ are of smaller area than the four triangular faces that are normal to $\langle\bar{1}\bar{1}\bar{1}\rangle$. In the Bevan model (Table 2), all eight faces have the same area.

3.2. The centre of the cluster

A Fourier map of the immediate environment of the cluster centre showed that this site [which corresponds to the 12(*b*) site in Table 3] is not occupied. Instead, peaks in the Fourier map were revealed along the four ⟨111⟩ directions from the

Table 4
Supercell at 503 K; space group $I\bar{4}3d$; a_0 = 21.805 (5) Å; R = 8.0%.

Parameters	Refined value	Atoms
a_1	0.0032 (3)	U2, U3
a_2	0.0030 (3)	U4, U5
a_3	0.0054 (4)	U6
a_4	0.0016 (4)	U7
$U_{\rm iso}$ for all U atoms (Å^2)	0.0054 (3)	U1–U7
b_1	0.0948 (2)	O1, O2, O3
b_2	0.0079 (3)	O1, O2, O3
b_3	0.0040 (4)	O6
b_4	0.0073 (2)	O7–O12
b_5	0.0014 (4)	O7, O8, O10
b_6	0.0013 (4)	O9, O11, O12
b_7	0.0017 (5)	O13
b_8	0.016 (1)	O15
$U_{\rm iso}$ for all O atoms (Å^2)	0.0110 (4)	O1–O15

centre, and displaced from the centre by about 0.64 Å. Thus, O15 is an atom occupying one of the four tetrahedral sites that are displaced by 0.64 Å from the centre. These atoms correspond to the O″ atoms displaced along ⟨111⟩ in the average cell of Table 1. To preserve the overall cubic symmetry of the β phase, the four sites are chosen at random throughout the crystal, so that there is a residual disorder that is removed in the low-temperature α phase (Willis & Cooper, 2004).

3.3. First shell of U atoms

A U atom is situated above each face of the cuboctahedron of O atoms. Above the square faces in the ⟨100⟩ direction from the cluster centre, U4 and U5 form an octahedron. Above the triangular faces, in the ⟨111⟩ directions, U6 and U7 form two independent tetrahedra. The position of U4 is constrained by the space-group symmetry as it is situated on a twofold axis. In the refinement, only the x parameter can be varied and, when coupled with the z parameter of U5 (a_2), this corresponds to an expansion of the U4–U5 octahedron. U6 and U7 are independent of one another – one parameter defines the movement of each atom along the ⟨111⟩ (a_3) and $\langle\bar{1}\bar{1}\bar{1}\rangle$ (a_4) directions, respectively, from the cluster centre.

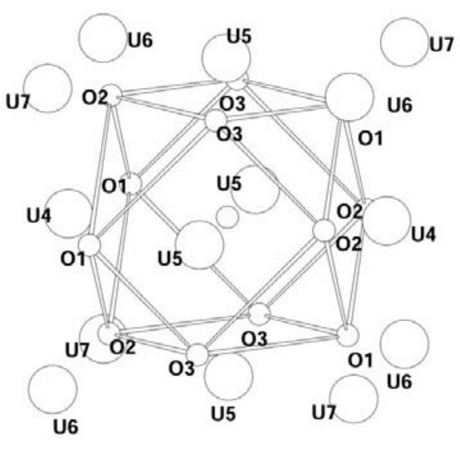

Figure 2
Cuboctahedral cluster of O atoms and first shell of U atoms.

3.4. Outer shells of O and U atoms

The next shell of 24 O atoms forms a hexatetrahedron, *i.e.* a cube truncated by two tetrahedra (see Fig. 3). This hexatetrahedron is centred on the 12-fold sites [12(b)] and is formed by the atoms O(7)–O(12) in Table 2. Three parameters may be refined, one corresponding to an overall expansion or contraction of the shell (b_4) and two parameters defining the expansion (b_5) or contraction (b_6) of the faces perpendicular to the ⟨111⟩ and $\langle\bar{1}\bar{1}\bar{1}\rangle$ directions, respectively.

Outside this shell, there are four remaining O atoms, all at or near the fluorite positions. O4 and O5 lie on the threefold axes and there is no scope for moving them without breaking the $\bar{4}3m$ cluster symmetry. O6 and O13 are in general positions and analysis shows that they may be independently displaced along $\langle\bar{1}\bar{1}\bar{1}\rangle$ (b_3 and b_7). Similarly, of the remaining U atoms, U1 lies on a threefold axis and cannot be moved during the refinement, while the x parameter of U2 may be varied along with the y parameter of U3 (a_1).

3.5. Atomic displacement parameters

The refined values of $U_{\rm iso}$ in Table 4 are only slightly larger than those calculated from lattice-dynamical considerations for UO_2 at 503 K (Dolling *et al.*, 1965). Clearly these parameters are thermal displacements. On the other hand, the $U_{\rm iso}$ values in Table 1 for the average cell are almost twice as large, and this is accounted for by the additional displacements of the atoms, as indicated in Table 4, from their ideal fluorite positions.

4. Crystal structure at 773 K

The 773 K data consisted of 39 fundamental and 374 superlattice reflections. In the range of $\sin\theta/\lambda$ covered in the experiment, there were approximately 90 reflections that were 'forbidden' on account of the 12(b) special extinction conditions. However, unlike the data at 503 K, seven of these 'forbidden' reflections were actually observed, and two of them (21, 19, 0 and 23, 16, 9) were more intense than the

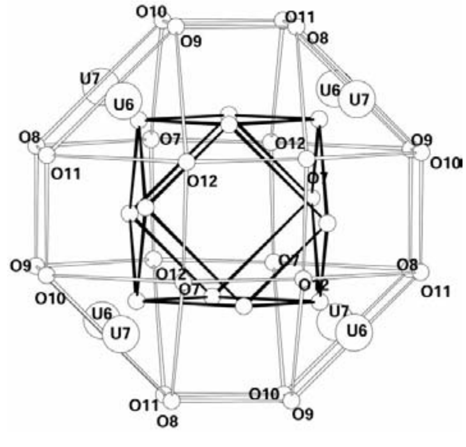

Figure 3
Hexatetrahedron of 24 O atoms surrounding the cuboctahedral cluster of 12 O atoms shown as heavier lines.

Table 5
Average cell at 773 K; space group $F\bar{4}3m$; a_0 = 5.468 (2) Å; R = 3.3%.

	Site	x	y	z	Occupancy	Total number	$U_{\rm iso}$ (Å^2)
U	4(a)	0	0	0	1.0	4	0.0135 (3)
O	4(c)	0.25	0.25	0.25	0.792 (5)	6.34 (4)	0.0280 (5)
O	4(d)	0.75	0.75	0.75			
O′	48(h)	$x = y$ = 0.625 (2)		0.5	0.0450 (17)	2.16 (8)	
O″	16(e)	$x = y = z$ = 0.604 (4)			0.028 (4)	0.45 (6)	

overall average of the superlattice reflections. Nevertheless, the 12(b) special symmetry constraints on the model have been left in place for the following refinement.

4.1. Fundamental reflections: contents of ‘average cell’ at 773 K

Analysis of 39 fundamental reflections alone yielded the contents of the ‘average cell’, as given in Table 5. These results are similar to those in Table 1 at 503 K. Again, the 4(b) site [corresponding to the 12(b) site in the supercell] is unoccupied.

4.2. All reflections: structure at 773 K

The refinement of the complete data set gave the parameters in Table 6.

There is a slight contraction of the cuboctahedral cluster of O atoms (b_2 = 0.0062) relative to the 503 K structure (b_2 = 0.0079) but no significant change in the skewing of the cluster (b_1 = 0.0943) compared to 503 K (b_1 = 0.0948). For the hexatetrahedron O7–O12, parameter b_4 indicates an expansion of the cluster (ignoring thermal expansion) by about 0.046 (6) Å relative to 503 K, accompanied by an increase in the size of the faces perpendicular to $\langle 111\rangle$ (b_5) and a decrease in the size of the faces perpendicular to $\langle\bar{1}\bar{1}\bar{1}\rangle$ (b_6). As regards the xyz parameters of all the remaining atoms, there is very little significant change from 503 K.

5. Conclusions

U_4O_9 is an intermediate oxidation product of uranium dioxide, UO_2. The approximate structure of the β phase of U_4O_9 was determined by Bevan *et al.* (1986), who showed that the U atoms occupy positions close to those in the fluorite structure of UO_2 and that the additional O atoms are accommodated in cuboctahedral clusters centred on the 12(b) positions of the cubic space group $I\bar{4}3d$. Refinement of this model has shown that the most significant change concerns the centres of the clusters. In the original model, these are occupied by single O atoms, but in the refined structures at 503 and at 773 K they are unoccupied.

Table 6
Supercell at 773 K; space group $I\bar{4}3d$; a_0 = 21.870 (5) Å; R = 9.9%.

Parameters	Refined value	Atoms
a_1	0.0036 (3)	U2, U3
a_2	0.0032 (3)	U4, U5
a_3	0.0056 (4)	U6
a_4	0.0025 (4)	U7
$U_{\rm iso}$ for all U atoms (Å^2)	0.0093 (3)	U1–U7
b_1	0.0943 (2)	O1, O2, O3
b_2	0.0062 (3)	O1, O2, O3
b_3	0.0038 (4)	O6
b_4	0.0094 (2)	O7–O12
b_5	0.0028 (3)	O7, O8, O10
b_6	0.0024 (3)	O9, O11, O12
b_7	0.0023 (4)	O13
b_8	0.015 (1)	O15
$U_{\rm iso}$ for all O atoms (Å^2)	0.0167 (5)	O1–O15

The refined model explains a puzzling aspect of the earlier studies of UO_{2+x}. Murray & Willis (1990) showed that the solid solution accommodates O-atom clusters with two types of atom: one type is displaced along $\langle 110\rangle$ from the cation interstitial sites of UO_2 and the other is displaced along $\langle 111\rangle$. The Bevan model in Table 2 accounts for the first type of atom but not the second, whereas the refined model identifies the missing atom as O15 in Table 3. The appearance at 773 K of superlattice reflections that are forbidden at 503 K may indicate that the cuboctahedral clusters are beginning to break up at the higher temperature.

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