

The Crystal Structure of β - U_4O_{9-y}

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The structure of the β form of U_4O_{9-y} , an anion-excess fluorite-related phase stable above 80°C, has been determined from the analysis of single-crystal neutron diffraction data collected at 230 and 500°C. The excess anions are accommodated in 13-member clusters which are centered on the 12-fold positions of the $I\bar{4}3d$ space group. The clusters are formed by the corner-sharing of octahedral groupings of UO_8 square antiprisms, which enclose a cuboctahedron of anions with an additional oxygen at the center. The unit cell composition is $U_{256}O_{572}$, i.e., U_4O_{9-y} with $y = 0.062$. © 1986 Academic Press, Inc.

Introduction

The existence of a new anion-excess fluorite-related phase in the uranium-oxygen system was first reported by Alberman and Anderson (1). It was characterized as having a composition $UO_{2.25}$, i.e., U_4O_9 , by Hering and Perio (2). Figure 1 shows a portion of a composite uranium-oxygen phase diagram encompassing the so-called U_4O_9 phase (3): it was derived from data extant prior to 1974. In this diagram the U_4O_9 phase is shown as being nonstoichiometric, U_4O_{9-y} , with an oxygen-rich boundary that

is both invariant with temperature and has the stoichiometric composition U_4O_9 ($y = 0$). However, in a more recent comprehensive review (4), careful assessment of the evidence available leads to the conclusion that stoichiometric U_4O_9 does not exist. For example, the results of Van Lierde, Pelsmaekers, and LeCocq-Robert (5) suggest that the composition range at room temperature is $0.020 < y < 0.060$ ($O:U = 2.235:2.245$), and at 1100°C it is $0.040 < y < 0.060$ ($O:U = 2.235:2.240$).

The phase diagram also reflects the existence of three polymorphs of U_4O_{9-y} : within the single-phase field two phase boundaries are crossed with increasing

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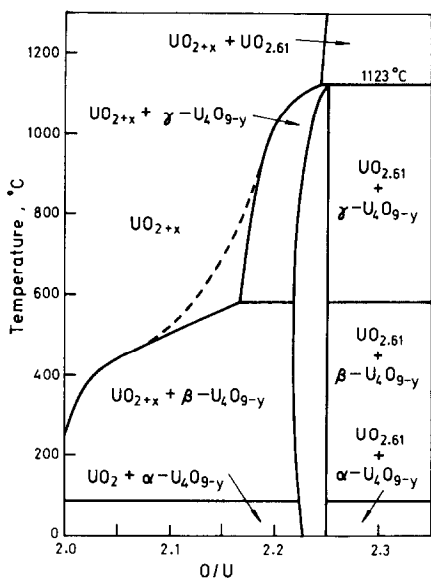


FIG. 1. Portion of a composite uranium-oxygen phase diagram encompassing U_4O_9 , from Ref. (4).

temperature, the α/β boundary at 80°C and the β/γ boundary at about 600°C.

In addition to the many phase studies, numerous attempts have been made during the last 20 years to derive the crystal structure of α - U_4O_{9-y} , assuming the unit cell to be cubic and the composition to be stoichiometric, U_4O_9 : such diverse methods as X-ray diffraction (6), neutron diffraction (7), X-ray photoelectron spectroscopy (8), and lattice energy calculations (9) have been used. In spite of all this activity, the detailed atomic arrangement in the α -phase is still unknown: the various models proposed are either inconsistent with or have not been tested against the experimental diffraction data of Willis (10). His results showed, by Fourier analysis of the fundamental reflections only, that the *average* fluorite-type unit cell ($a \approx 5.4 \text{ \AA}$) contained some vacancies at normal anion sites and two types of interstitial oxygen, each sited about 1 \AA from the empty octahedral site of the fcc cation array along $\langle 110 \rangle$ (O') and $\langle 111 \rangle$ (O''), respectively. The models are also inconsistent with our own unpublished

neutron-diffraction data on the superlattice intensities of the α -phase.

There is some evidence that the true unit cell of the α -phase is slightly distorted from cubic to rhombohedral symmetry (11), giving the possibility of domain formation (12) or fine-scale twinning when the phase is formed by cooling from high temperature, and this may be a principal cause for the failure to solve its structure. However, the β -phase, whose structure is closely related to that of the α -phase, is strictly cubic, and we now present a preliminary report of the successful determination of its crystal structure by single-crystal neutron diffraction. A full account of experimental and computational procedures will be given subsequently.

Experimental

Single crystals of U_4O_9 were prepared by oxidation of large single crystals of UO_2 as follows. The UO_2 crystals were first ground into spheres of 2-mm diameter and then purified in a stream of hydrogen gas at 1000°C for 10 hr. Each crystal was subsequently placed in one arm of an evacuated quartz H-tube with powdered U_3O_8 in the other arm. After heating for one month at 1100°C, the oxygen atoms released from thermal dissociation of U_3O_8 diffused into the UO_2 to yield spherical crystals of composition U_4O_{9-y} .

Neutron diffraction intensities were collected from three of these crystals, using the D9 diffractometer at the Institut Laue-Langevin, Grenoble. The first two crystals were measured at 230°C and the third at 500°C.

In agreement with the X-ray work of Belbeoch *et al.* (11) the space group was found to be $I43d$. The β phase is an ordered superstructure, giving fundamental and superlattice intensities based on a 21.9- \AA unit cell composed from $4 \times 4 \times 4$ fluorite-type subcells.

Solution of the Structure

Structural Principle

To solve the structure it is necessary to determine the phases of the superlattice reflections. However, the domination of the intensity data by the strong fluorite subcell reflections, together with the inherent difficulties associated with a large, high-symmetry unit cell, prohibits the use of standard crystallographic techniques for the phasing, and we have been forced to seek new model structures for testing. In this we were guided by the extensive data available for complex fluorides. Bevan, Greis and Strahle (13) have observed that many of these fluorite-related, anion-excess superstructures contain octahedral groupings of MF_8 square-antiprisms which share corners to enclose a cuboctahedron of anions. In different structures the cuboctahedron is either empty, or filled with an extra anion, giving rise to M_6F_{36} or M_6F_{37} clusters containing 4 or 5 excess fluorines per cluster relative to the fluorite analogue, M_6F_{32} . Aléonard, LeFur, Pontonnier, Gorius, and Roux (14) had previously noted that the conversion of a cube to a square-antiprism is a fundamental first step in the formation of anion-excess, fluorite-related phases.

Such clusters have not previously been reported in oxides, presumably because their formation is less favorable energetically vis-à-vis fluorides, but their existence is not excluded. Figure 2 shows schematically the fluorite structure viewed along [001]: the formation of an isolated U_6O_{36} cluster is depicted. For simplicity, the only uranium atoms shown are those at $Z_f = 0$, which is the plane passing through the center of the cluster. (The subscript "f" refers to the fluorite subcell.) The 12 anions forming the cuboctahedral vertices are labelled C' ($Z_f = 0$) and C ($Z_f = \pm 0.38$) in Fig. 2, and are displaced by approximately $\frac{1}{5}\langle 110 \rangle_f$, i.e., about 1 Å, from the nearest, empty octahedral sites in the cation array: *they are the O'*

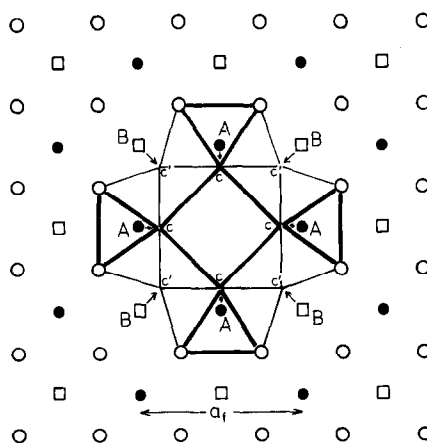


FIG. 2. The fluorite structure viewed along a four-fold axis, showing an isolated U_6O_{36} cluster. Cations and interstitial octahedral sites at $Z_f = 0$ are represented by filled circles and open squares, respectively. Lattice anions are shown by open circles, and the anions forming the cuboctahedron are labeled C' ($Z_f = 0$) and C ($Z_f = \pm 0.38$).

interstitials previously described by Willis, and, indeed, Fourier analysis of the fundamental reflection intensities of the new data confirm the presence of O' interstitials. It is important to note that this result is quite independent of any model and derives solely from the data.

Patterson Maps

The Patterson synthesis is another source of model-independent information which can be obtained without knowing the phases of the superlattice reflections. In the case of U_4O_{9-y} , a conventional Patterson synthesis is of limited value for determining the superstructure, as it is dominated by the strong fluorite subcell vectors. However, in a partial Patterson map, obtained using only the superlattice reflections, these vectors are effectively removed and what remain are the vectors between atoms on sites that deviate significantly from fluorite sites. Table I gives a list of such vectors. The positive peaks are readily identified as intervertex vectors

TABLE I
PARTIAL PATTERSON PEAKS

| Peak height | Coordinates | | | | | |
|-------------------|-------------|----------|----------|-------------------------------|----------|--------------------|
| | Observed | | | Calculated from ideal cluster | | |
| | <i>u</i> | <i>v</i> | <i>w</i> | <i>u</i> | <i>v</i> | <i>w</i> |
| 100 | 0.094 | 0.094 | 0.000 | 0.087 | 0.087 | 0 ^a |
| 91 | 0.189 | 0.000 | 0.000 | 0.174 | 0 | 0 ^a |
| 52 | 0.184 | 0.091 | 0.091 | 0.174 | 0.087 | 0.087 ^a |
| 28 | 0.188 | 0.000 | 0.188 | 0.189 | 0 | 0.189 ^a |
| 32 | 0.156 | 0.110 | 0.063 | 0.151 | 0.105 | 0.063 ^b |
| 29 | 0.066 | 0.111 | 0.030 | 0.063 | 0.105 | 0.026 ^b |
| -218 ^d | 0.000 | 0.261 | 0.000 | 0 | 0.256 | 0 ^c |
| -139 ^d | 0.118 | 0.260 | 0.000 | 0.125 | 0.256 | 0 ^c |
| -76 | 0.000 | 0.148 | 0.000 | 0 | 0.131 | 0 ^c |
| -53 | 0.121 | 0.144 | 0.000 | 0.125 | 0.131 | 0 ^c |
| -35 | 0.020 | 0.020 | 0.058 | 0.026 | 0.026 | 0.063 ^c |

^a Intervortex vectors for a cuboctahedron of oxygen atoms in the U_4O_{9-y} supercell.

^b Intervortex vectors for the square antiprisms, UO_8 , which share corners to enclose the cuboctahedron.

^c Vectors between cluster oxygens and the formal subcell vacancies.

^d These peaks contain contributions from noncluster atoms.

for the square antiprism cluster, divided into two groups, *viz.* the cuboctahedral and other square antiprism vectors (half of the latter are subcell vectors and cannot be identified). The negative peaks are the vectors between cluster oxygens and the oxygen "vacancies" of the subcell.

Possible Models Based on U_6O_{36} or U_6O_{37} Clusters

In view of the support for a cluster model obtained from the partial Patterson synthesis, a study was made of possible arrangements of clusters in the β - U_4O_{9-y} superlattice, consistent with the known space group, $I43d$. The clusters may be centered on threefold axes, positions 16(c), or on 4 axes, positions 12(a) or 12(b).

(i) Clusters Centered on Threefold Axes

Each U_6O_{36} cluster corresponds to four extra anions and so 16 clusters centered on 16(c) give rise to 64 extra anions, the exact number required for stoichiometric U_4O_9 .

U_6O_{37} clusters must be excluded on compositional grounds.

There are three different models, corresponding to clusters centered on $(x\ x\ x)$ with $x = 0, \frac{1}{8}$ and $\frac{1}{4}$. The origin of the unit cell is chosen on a threefold axis, halfway between three pairs of nonintersecting 2 axes. The three models are shown in projection along [001] in Figs. 3a-c.

For $x = 0$, the model comprises isolated clusters. The model can be described in a $2 \times 2 \times 2$ body-centered fluorite supercell, and so is not consistent with the diffraction data, for which many of the strongest superlattice reflections have odd indices.

For $x = \frac{1}{8}$ the U_6O_{36} clusters are not isolated. Three antiprisms in each cluster share an edge with antiprisms in adjacent clusters.

For $x = \frac{1}{4}$ double-edge sharing occurs between clusters. The edge-linked groups form chimney spirals along [100].

(ii) Clusters Centered on $\bar{4}$

Figure 3d corresponds to clusters centered on the 12(b) sites; the enantiomorphous structure is obtained for clusters centered on 12(a) sites. Twelve U_6O_{36} clusters give only 48 extra anions per unit cell ($UO_{2.1875}$), a composition which is quite outside the single-phase field. However, if the clusters are U_6O_{37} , with each cuboctahedron filled, there are 60 extra anions per unit cell, and the composition is $U_{256}O_{572}$ or $UO_{2.2344}$, the lower boundary of the U_4O_{9-y} field.

Testing of Models

Our neutron data for all three crystals were used to test the four models described above. A satisfactory refinement was possible only for the last model, with clusters centered on $\bar{4}$. This result is consistent with the observation, first made by Blank and Ronchi (15), that the superlattice reflections all obey the special extinction rules for the $\bar{4}$ sites of space group $I43d$.

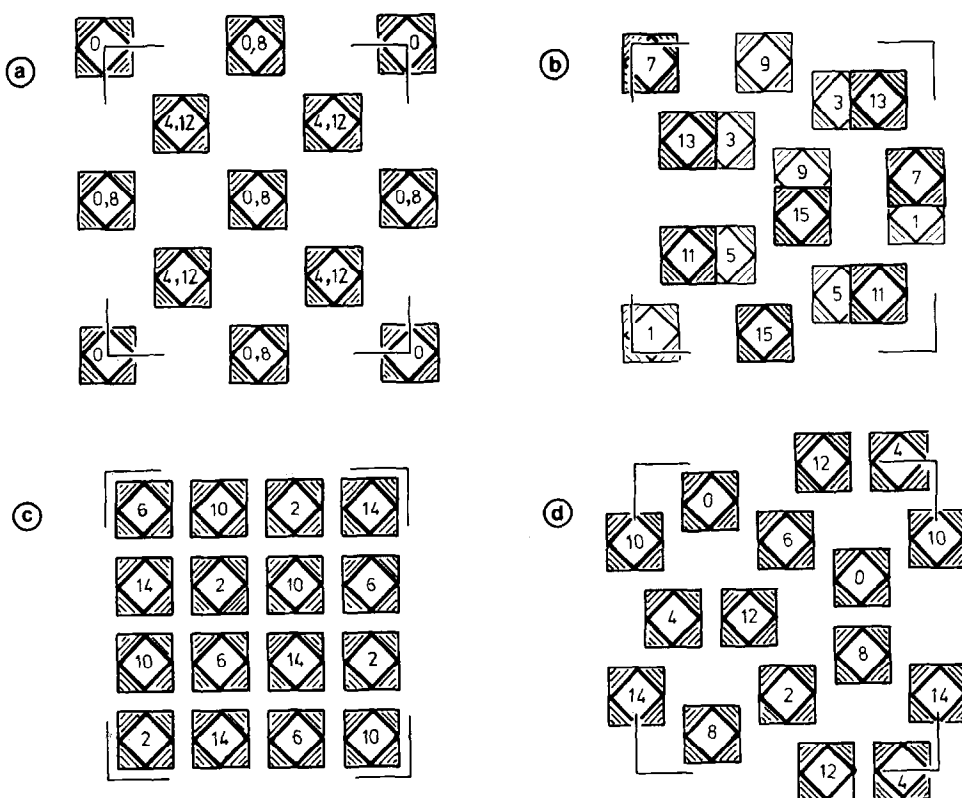


FIG. 3. Schematic representation of possible models for U_4O_9 , based on ordering of U_6O_{36} and U_6O_{37} clusters on the special positions of $I43d$. The outlines of the cuboctahedra enclosed by each cluster are shown. Numbers given the z coordinates of the cluster centers in sixteenths of the supercell (21.9 \AA). The centers of the U_6O_{36} clusters are at 16(c) sites with coordinates $(x x x)$: (a) $x = 0$; (b) $x = \frac{1}{16}$; (c) $x = \frac{1}{4}$. The U_6O_{37} clusters are centered on 12(b) sites: (d).

This implies that whatever the main perturbation of the anion sublattice may be, it is centered on one of these sites, either 12(a) or 12(b).

The chosen model is also consistent with the analysis of the fundamental reflections, although recently (16) some doubt has been thrown on the reliability of this technique, particularly with regard to the population parameters of the interstitial atoms. The results are shown in Table II.

The refinement of the structure to an R factor less than 10% will be reported subsequently. A constrained refinement of this model, in which clusters centered on 12(b) sites are allowed to relax while still retain-

TABLE II
STRUCTURAL PARAMETERS OF AVERAGE SUBCELL
OF $\beta\text{-U}_4\text{O}_{9-y}$

| Atom | Atomic coordinates | | | Composition number | |
|-------------------------|--------------------|-------------------|-------------------|--------------------|-------|
| | | | | Data analysis | Model |
| Uranium | 0 | 0 | 0 | 1.00 | 1.00 |
| Normal oxygen O | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 1.45 ± 0.12 | 1.625 |
| Interstitial oxygen O' | $\frac{1}{2}$ | $\frac{1}{2} + v$ | $\frac{1}{2} + v$ | 0.70 ± 0.05 | 0.56 |
| Interstitial oxygen O'' | $\frac{1}{2} + w$ | $\frac{1}{2} + w$ | $\frac{1}{2} + w$ | 0.07 ± 0.03 | 0.047 |

Note. $v = 0.132 \pm 0.002$, $w = 0.125 \pm 0.002$.

ing the $m3m$ cubic point symmetry of an isolated ideal cluster, gives an R factor of 16% with just four variable positional parameters (see Table III). Indeed, even using the original room-temperature superlattice data for the α -phase, we had already obtained convincing evidence for this model.

Lattice energy calculations on the cuboctahedral cluster have been carried out by J. Harding (private communication, 1984) using the HADES computer code (17, 18). These calculations show that the cluster is stable in the fluorite framework of UO_2 , and that the positions of the twelve oxygen ions which are nearest to the cluster center (the O' interstitials along $\langle 110 \rangle$: atoms O(1), O(2), O(3) in Table III) agree almost exactly with the observed positions. Further work is in progress using HADES to calculate the displacements of the more distant ions in the cluster, and these results will be reported later.

TABLE III
POSITIONAL PARAMETERS (WITH esd's IN PARENTHESES) FOR CLUSTERS WITH CUBIC POINT SYMMETRY

| Atom | Position | x | y | z |
|-------|----------|---------|--------|--------|
| U(1) | 16(c) | 0 | 0 | 0 |
| U(2) | 24(d) | 0.25 | 0 | 0.25 |
| U(3) | 48(e) | 0.125 | 0.125 | 0.25 |
| U(4) | 24(d) | 0.003 | 0 | 0.25 |
| U(5) | 48(e) | -0.125 | 0 | 0.121 |
| U(6) | 48(e) | -0.004 | 0.121 | 0.371 |
| U(7) | 48(e) | -0.004 | 0.121 | 0.129 |
| O(1) | 48(e) | -0.030 | 0.094 | 0.25 |
| O(2) | 48(e) | -0.030 | 0 | 0.344 |
| O(3) | 48(e) | -0.125 | 0.094 | 0.344 |
| O(4) | 16(c) | 0.0625 | 0.0625 | 0.0625 |
| O(5) | 16(c) | 0.1875 | 0.1875 | 0.1875 |
| O(6) | 48(e) | 0.0625 | 0.1875 | 0.1875 |
| O(7) | 48(e) | 0.072 | 0.0625 | 0.1875 |
| O(8) | 48(e) | -0.0625 | 0.0625 | 0.052 |
| O(9) | 48(e) | -0.0625 | 0.0625 | 0.4375 |
| O(10) | 48(e) | -0.0625 | 0.197 | 0.1875 |
| O(11) | 48(e) | -0.0625 | 0.197 | 0.3125 |
| O(12) | 48(e) | 0.072 | 0.0625 | 0.3125 |
| O(13) | 48(e) | -0.0625 | 0.1875 | 0.4375 |
| O(14) | 12(b) | -0.125 | 0 | 0.25 |

Description of the Structure

The distribution of U_6O_{37} clusters in the unit cell of $\beta\text{-U}_4\text{O}_{9-y}$ is shown in Fig. 3d. Each cluster is discrete. Nearest-neighbor clusters are separated by $\frac{1}{2}\langle 123 \rangle_f$, and the link between them in the structure is effected through pairs of edge-sharing empty cubes, each of which shares a face with a square antiprism from separate clusters. The next-nearest-neighbor vector is $\langle 120 \rangle_f$.

Each cluster contains six U-centered square antiprisms which are surrounded by eight 10-coordinated U sites: in $\beta\text{-U}_4\text{O}_{9-y}$ none of these is common to two or more clusters. Thus, in summary, the structure contains twelve U_6O_{37} clusters per unit cell, or 72 U atoms in 9-coordination inside monocapped square antiprisms, 96 U atoms in 10-coordination, and the remainder (88) in 8-fold cubic coordination. Just how U^{4+} , U^{5+} and, even, perhaps, U^{6+} cations are distributed over these sites is a matter for further study.

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