

A Neutron Diffraction Study of Anion Clusters in Nonstoichiometric Uranium Dioxide

A. D. MURRAY

*Computer Centre, University College London, Gower Street,
London WC1E 6BT, United Kingdom*

AND B. T. M. WILLIS*

*Chemical Crystallography Laboratory, 9 Parks Road,
Oxford OX1 3PD, United Kingdom*

Received April 26, 1989; in revised form August 21, 1989

Neutron diffraction data have been collected at 970 K on single crystals of $\text{UO}_{2.11}$ and $\text{UO}_{2.13}$. The data were more extensive than those obtained in an earlier neutron study of $\text{UO}_{2.12}$ and were measured at a shorter wavelength, allowing TDS corrections to be made to the Bragg intensities. The new results support the concept that the oxidation of UO_2 proceeds by the formation of anion vacancies and of two types of oxygen interstitial. One type is displaced along $\langle 110 \rangle$ from the anion sites in UO_2 and the other is displaced along $\langle 111 \rangle$. In the first crystal the occupation numbers of the three kinds of oxygen defect are close to those expected from the formation of 2:2:2 clusters, whereas for the second crystal the occupation numbers correspond to those calculated for cuboctahedral clusters. © 1990 Academic Press, Inc.

1. Introduction

The structure of the nonstoichiometric phase, UO_{2+x} , of uranium dioxide was examined 25 years ago by Willis (1) using single-crystal neutron diffraction. He found that the fluorite framework of $\text{UO}_{2.00}$ is preserved during oxidation and that the extra oxygens occupy two types of interstitial site within this framework. One type (labeled O') is displaced by about 1 Å from a normal fluorite site and along a $\langle 110 \rangle$ direction, whereas the other type (O'') is displaced by about the same amount along $\langle 111 \rangle$. The formation of these interstitials is

accompanied by the creation of anion vacancies. These experimental results led to the concept that the oxidation of UO_2 proceeds through the formation of groups of defect atoms (or "defect clusters") in the anion fluorite sublattice, without any corresponding structural change in the cation sublattice. From the observed "occupation numbers" of the atoms, it was tentatively suggested that each cluster contains two O' interstitials, two O'' interstitials, and two normal oxygen vacancies; this is known as the 2:2:2 cluster and is illustrated in Fig. 1.

A puzzling aspect of the 2:2:2 cluster is the short oxygen–oxygen contact (~ 2 Å) between neighboring O' interstitials. This

* To whom correspondence should be addressed.

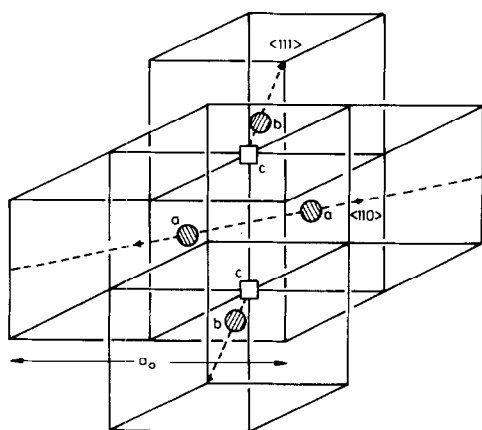


FIG. 1. The 2:2:2 cluster. The corners of the cubes are the sites of normal oxygen atoms. The cluster contains two O' oxygens (indicated by a), two O'' oxygens (b), and two vacant anion sites (c). a_0 is the edge of the fluorite cell.

difficulty is avoided in the more complex configuration, known as the U_6O_{37} cluster or "cuboctahedral cluster," which is described by Bevan *et al.* (2). It is formed by corner-sharing of octahedral groupings of UO_8 square antiprisms, enclosing a cuboctahedron of anions with an additional oxygen at the center. This cluster is illustrated in Fig. 2.

The aim of the present study was to extend the earlier diffraction study of Willis, in order to determine whether the anion clusters in nonstoichiometric UO_{2+x} conform to the 2:2:2 type or to the cuboctahedral type. This requires the occupation numbers to be derived with high precision, so that the intensity measurements must be as accurate as possible. Compared with the situation in 1963, much better measurements are possible today, using the neutron-scattering apparatus at the Institut Laue Langevin in Grenoble.

2. Experimental Work

(a) Preparation of Samples

The samples consisted of small spherical crystals of U_4O_9 weighing between 60 and

350 mg. These were produced from crystals of UO_2 , which had been grown using the vapor deposition technique (3). The UO_2 was oxidized to U_4O_9 , and the crystals then ground to spherical shapes with a Bond sphere grinder. Finally, reduction of the samples, to give an oxygen-to-metal ratio lying in the range 2.10 to 2.20, was achieved by heating in a tube furnace, in a continuously flowing hydrogen-nitrogen gas mixture at 800°C .

Accurate weighing of the heavier samples revealed a weight reduction from U_4O_9 of about 1%, corresponding to a change in the U/O ratio of 5%. (More accurate methods of deriving the stoichiometry require the controlled reduction to a known composition and measurement of the corresponding changes of weight.)

The samples were sealed in evacuated silica capillaries and held rigidly in position with silica wool. Quartz is almost transparent to thermal neutrons, and so absorption and scattering by the silica can be ignored.

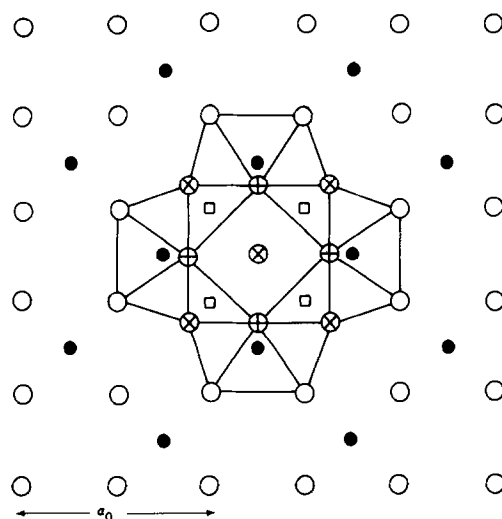


FIG. 2. The cuboctahedral cluster. The atomic symbols and the z -coordinates of the atoms, in units of the cell edge (a_0), are as follows: (○) normal oxygens at $z = \pm\frac{1}{4}$; (●) uraniums at $z = 0$; (⊗) oxygen interstitials at $z = 0$; (⊕) oxygen interstitials at $z = \pm 1/(2\sqrt{2})$; (□) oxygen vacancies at $z = \pm\frac{1}{4}$.

(b) Measurement of Bragg Intensities

Data were measured using the D9 four-circle diffractometer at the ILL in Grenoble. A short wavelength of 0.54 Å was selected, in order to permit a correction for thermal diffuse scattering (see Section 3a). The samples were mounted vertically in a specially constructed goniometer and heated with hot air blown along the path of the incoming neutron beam, using the D9 "soufflette" furnace.

Temperature calibration was carried out by means of two thermocouples, one located at the sample position inside the silica tube and the other in the hot air stream outside the tube. Although air temperatures exceeding 900°C could be attained, the thermal gradient across the wall of the silica tube limited the maximum sample temperature to 700°C. The transition temperature from the two-phase $\text{UO}_2 + \text{U}_4\text{O}_9$ to the single-phase UO_{2+x} rises with increasing x , and so data collection was restricted to the two samples (crystal A of 67 mg and crystal B of 276 mg) with the lowest oxygen-to-uranium ratios. Both samples showed traces of superlattice reflections from U_4O_9 , but the analysis was carried out assuming that the measurements were entirely in the single-phase nonstoichiometric region.

In toto, 675 reflections were measured for sample A and 930 for sample B. Symmetry-equivalent reflections were then averaged to yield 60 independent structure factors for A and 81 for B. The standard error of the structure factors was estimated from the spread in values of equivalent reflections. (For both crystals this error was always less than 2%.) The space group was confirmed to be $Fm\bar{3}m$ from systematic absences, and the temperature of the samples during the measurements was estimated to be 970 K. Determination of the O/U ratio was more difficult: by noting the changes on oxidation in both the weight and the size of the unit cell, we considered that the O/U

ratio was 2.11 for sample A and 2.13 for sample B.

3. Data Analysis*(a) Correction for Thermal Diffuse Scattering*

Before the analysis proper of the data could begin, it was necessary to correct the Bragg intensities for the contribution from thermal diffuse scattering (TDS). Such a correction is only feasible with neutrons if the neutron velocity exceeds the maximum value of the sound velocity in the crystal. At 970 K the elastic stiffness coefficients of UO_2 are $c_{11} = 33.0$, $c_{12} = 11.5$, $c_{44} = 6.0$, all in units of 10^{11} dyn cm^{-2} (4). We can calculate from these measurements that the sound velocity attains its maximum value of 5.6 km sec^{-1} for the propagation of longitudinal acoustic modes along $\langle 100 \rangle$ and that the neutron wavelength corresponding to this velocity is 0.70 Å. The effect of increasing the O/U ratio above 2.0 is to reduce the longitudinal velocities even further (5), and the critical wavelength then rises above 0.70 Å.

In our experiment we chose a neutron wavelength of 0.54 Å. This is well below the critical value of 0.70 Å and so we were able to carry out a standard TDS correction using the computer program of Merisalo and Kurittu (6). The correction to the intensities varied from a few percent for the low-index Bragg reflections to 36% for high-index reflections.

No other corrections were made to the experimental data. Thus it was considered unnecessary to apply an extinction correction, because the incorporation of interstitial oxygens into the fluorite framework of UO_2 gives the crystal a large mosaic spread.

(b) Results from Least-Squares Analysis

The corrected intensities were converted to structure factors and then analyzed using

the least-squares program XFLS4 of Busing *et al.* (7). The variable parameters were the isotropic temperature factors of the uranium and oxygen atoms, the coordinates of the interstitial oxygens, their occupation numbers in the unit cell, and an overall scale factor. The interstitial oxygens occupied two kinds of site (*l*): O' sites displaced along $\langle 110 \rangle$ directions from the fluorite-type sites, and O'' sites displaced along $\langle 111 \rangle$. Fourier difference maps confirmed that there were no other kinds of oxygen site.

In order to take into account the effect of anharmonic contributions to the temperature factors, a third cumulant coefficient c_{123} (8) was introduced for the oxygen atoms. No such coefficient was needed for the uraniums, because these atoms occupy centro-symmetric sites and so are constrained by symmetry to vibrate isotropically. There are 10 third-cumulant coefficients for oxygen, but the symmetry of the $Fm\bar{3}m$ space group reduces nine of them to zero, leaving just one parameter, c_{123} , to be determined from the measurements.

The importance of including anharmonicity in the analysis can be readily judged by referring to Table I. This shows the comparison between observed (I_0) and calculated (I_c) intensities when anharmonic vibrations are allowed ($c_{123} \neq 0$) and are not allowed ($c_{123} = 0$). Anharmonicity affects the calculated values of odd-index reflections only, and so even-index reflections are omitted from the table.

The second column in the table gives the observed Bragg intensity (on an arbitrary scale) and the third column the calculated intensity without third cumulants. The difference between these two intensities (fourth column) is positive if $h + k + l = 4n + 1$ and is negative if $h + k + l = 4n - 1$; this is exactly the behavior that is predicted by the general anharmonic theory (8). The last column gives the intensity difference when third cumulants are included. Defining an R factor as the ratio

$$R = \frac{\sum(I_0 - I_c)}{\sum I_0},$$

we find that $R = 17.2\%$ (for 13 reflections) with $c_{123} = 0$. For $c_{123} = 0.0003$, R is 1.7%, which is a great improvement.

Table II lists the parameters derived from the least-squares comparison of calculated and observed structure factors. They are of three kinds, viz. vibrational parameters, including third-cumulant coefficients; positional coordinates of the two types of interstitial oxygen; and occupation numbers of the interstitial oxygens and of the oxygens occupying normal fluorite-type sites.

The vibrational parameters B_U and B_O in Table II are defined by

$$B_U = 8\pi^2 \overline{u_U^2} \quad \text{and} \quad B_O = 8\pi^2 \overline{u_O^2},$$

where $\overline{u_U^2}$ ($\overline{u_O^2}$) are the mean-square displacements of uranium (oxygen) atoms from their ideal fluorite sites. The positional parameters, v and w , are defined in Section 4(b). Finally, the occupation numbers are expressed in terms of the contribution of the atom to the formula unit, UO_{2+x} . Thus

TABLE I
EFFECT OF THIRD CUMULANTS ON MAGNITUDES
OF DIFFRACTION PEAKS

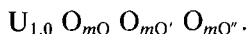
<i>hkl</i>	I_0	I_c	$I_0 - I_c$ (without c_{123})	$h + k + l$ $= 4n \pm 1$	$I_0 - I_c$ (with c_{123})
333	21.5	18.8	+2.7	+	0.2
533	12.3	13.4	-1.1	-	0.2
733	12.0	9.6	+2.4	+	0.6
933	4.0	4.6	-0.6	-	0.0
11,3,3	2.1	1.8	+0.3	+	0.0
553	12.6	9.8	+2.8	+	0.0
753	5.4	6.5	-1.1	-	0.0
11,5,3	0.8	1.1	-0.3	-	-0.1
773	5.0	3.9	+1.1	+	0.0
973	1.5	1.8	-0.3	-	0.0
555	5.5	6.9	-1.4	-	0.0
755	5.9	4.6	+1.3	+	-0.3
955	1.9	2.1	-0.2	-	0.2

TABLE II
RESULTS FROM LEAST-SQUARES ANALYSIS OF CRYSTALS A AND B
(THIS STUDY) AND CRYSTAL C (REF. 1)

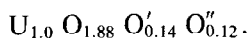
	Crystal A (O/U = 2.11)	Crystal B (O/U = 2.13)	Crystal C (O/U = 2.12)
(a) Vibrational parameters			
B_U (\AA^2):	1.15 (1)	1.32 (1)	1.18 (2)
B_O (\AA^2):	2.31 (4)	2.51 (2)	1.45 (4)
c_{123}	0.00027 (3)	0.00033 (2)	—
(b) Displacement parameters			
v : (O' oxygen)	0.36 (1)	0.37 (1)	0.38 (1)
w : (O'' oxygen)	0.36 (1)	0.35 (1)	0.41 (1)
(c) Occupation numbers			
m_O :	1.88 (2)	1.68 (1)	1.87 (3)
$m_{O'}$:	0.14 (3)	0.33 (2)	0.08 (4)
$m_{O''}$:	0.12 (2)	0.10 (2)	0.16 (6)

Note. R factor = 3.1% for 60 reflections (crystal A), 2.7% for 81 reflections (B), and 3.5% for 38 reflections (C).

the formula unit can be written as



Crystal A, for example, in Table II has the formula unit



This expression indicates that the uraniums are unchanged by oxidation, whereas 6% of the oxygens leave their fluorite sites and join the additional oxygens (which arise in the oxidation process) to occupy the two types of interstitial site.

4. Discussion

(a) Vibrational Parameters

For stoichiometric $UO_{2.0}$ at 970 K the B factors, which occur in the Debye-Waller expression $\exp(-B \sin^2 \theta / \lambda^2)$, are 0.75 \AA^2 for uranium and 1.55 \AA^2 for oxygen (8). These values are appreciably less than those listed in Table II. The B factors are proportional to the mean-square displacements of the atoms from their average positions, and so the difference between the two values can be ascribed to the contribu-

tion of static disorder to the atomic displacements in the nonstoichiometric oxides.

The measured value of c_{123} for stoichiometric $UO_{2.0}$ is 0.0010, which is larger than the estimates given in Table II. We do not have an explanation for this large difference between the oxides with O/U ratios of 2.0 and 2.1.

(b) Displacement Parameters

The parameter v in Table II refers to the positions of the interstitial O' atoms: these occupy the sites

$$(0.5, v, v)$$

—plus symmetry-related sites—in the cubic unit cell, where a uranium atom is placed at the cell origin. Similarly, w in Table II refers to interstitial atoms O'' occupying the sites

$$(w, w, w).$$

These two types of interstitial site are shown in Fig. 1.

The O' atoms are displaced along $\langle 110 \rangle$ from the large interstitial holes at (0.5, 0.5,

0.5) by an amount

$$\sqrt{2} \cdot 0.14 \cdot 5.49 \text{ \AA}$$

or 1.09 Å. The corresponding displacement of the O^o interstitials along $\langle 111 \rangle$ is

$$\sqrt{3} \cdot 0.14 \cdot 5.49 \text{ \AA}$$

or 1.33 Å. These displacements are equally consistent with the 2:2:2 cluster and the cuboctahedral cluster.

(c) Occupation Numbers

In principle, the occupation numbers of the three kinds of oxygen atom should provide the most convincing evidence for one kind of cluster or another. These numbers have been measured more precisely in crystals A and B than in crystal C, and yet, surprisingly, the numbers are quite different for the A and B crystals. The occupation numbers in Table II for crystal A are close to the values expected for 2:2:2 clusters, while those for B are similar to the values calculated for cuboctahedral clusters.

It appears that the type of defect cluster can vary from one sample to another, dependent on its composition, oxidation treatment, etc. Crystal B is significantly more defective than A, even though the oxygen/uranium ratios are nearly the same. To obtain further understanding of these fluorite

systems containing anion defects, it will be necessary to extend the type of observations described in this paper to many other points in the phase diagram of UO_{2+x} .

Acknowledgments

We thank Dr. M. S. Lehmann for his expert experimental guidance during the collection of the experimental data on the D9 diffractometer at the Institut Laue Langevin in Grenoble. Financial assistance was provided by the Science and Engineering Research Council of the United Kingdom, and the work was undertaken as part of the Underlying Research Programme of the UKAEA.

References

1. B. T. M. WILLIS, *Proc. Brit. Ceram. Soc.* **1**, 9 (1964).
2. D. J. M. BEVAN, I. E. GREY, AND B. T. M. WILLIS, *J. Solid State Chem.* **61**, 1 (1986).
3. W. VAN LIERDE, R. STRUMANE, E. SMETS, AND S. AMELINCKX, *J. Nucl. Mater.* **5**, 250 (1962).
4. K. CLAUSEN, W. HAYES, M. T. HUTCHINGS, J. K. KIEMS, J. E. MACDONALD, AND R. OSBORN, *High Temp. Sci.* **19**, 719 (1984).
5. R. DE BATIST, *Mater Res. Bull.* **1**, 75 (1966).
6. M. MERISALO AND J. KURITTU, *J. Appl. Crystallogr.* **11**, 179 (1978).
7. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, "ORXFLS4 Crystallographic Structure-Factor Least-Squares Program," Oak Ridge National Laboratory, (1984).
8. B. T. M. WILLIS AND R. G. HAZELL, *Acta Crystallogr. A* **36**, 582 (1980).