

The Defect Structure of Hyper-stoichiometric Uranium Dioxide

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Earlier neutron-diffraction measurements [Willis (1964), *Proc. Br. Ceram. Soc.* **1**, 9–19] on a single crystal of $\text{UO}_{2.12}$ at 800°C showed that interstitial oxygen atoms enter the UO_2 lattice at two kinds of site, which are displaced by about 1 \AA along the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions from the cubic-coordinated interstitial sites. It was also shown that the solution of oxygen is accompanied by the formation of vacancies in the normal oxygen sites, but that the uranium sublattice remains undisturbed. A new analysis of the same data has been carried out, which introduces constraints between some of the parameters and allows a more satisfactory treatment of the anharmonic motion of the oxygen atoms. The new analysis leads to a much more precise determination of the occupation numbers of the $\langle 110 \rangle$ and $\langle 111 \rangle$ oxygen atoms and of the normal oxygen vacancies. The simplest model to account for these new results is the so-called 2:2:2 configuration of oxygen defects.

1. Introduction

UO_2 is readily oxidized at high temperature to hyper-stoichiometric UO_{2+x} by the incorporation of additional oxygen atoms at interstitial sites of the cubic fluorite structure. Theoretical calculations (Catlow, 1974) indicate that for $x < 0.01$ the additional atoms occupy the cubic-coordinated sites representing the largest interstices in the fluorite structure. There are four of these interstices in the unit cell: see Fig. 1. Earlier neutron diffraction studies (Willis, 1964) carried out at a temperature of 800°C have shown that for $x = 0.12$ the additional atoms do not occupy these cubic-

coordinated sites. They occupy instead two types of interstitial site which are displaced from the cubic-coordinated sites by about 1 \AA in the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, respectively, leaving vacant sites in the normal oxygen sublattice. In order to account for the diffraction results, which consist essentially of the occupation numbers of the atoms in the average unit cell, it is necessary to postulate that the interstitial oxygen atoms are not distributed at random throughout the lattice but that they cluster together in defect clusters or complexes. Each complex contains $\langle 110 \rangle$ and $\langle 111 \rangle$ interstitial oxygen atoms, vacant normal oxygen sites and U^{5+} ions to maintain charge balance. There are no displacements of the uranium atoms from their fluorite positions, and indeed the occupation number of the cations remains the same as in the stoichiometric compound UO_2 . The earlier analysis (Willis, 1964; Roberts, 1965) considered several possible types of defect complex, involving different proportions of $\langle 110 \rangle$ and $\langle 111 \rangle$ interstitial oxygens, but the estimated standard deviations of the occupation numbers of the interstitial atoms were too large to allow the unambiguous selection of a particular type of complex.

We have now re-analysed the earlier data using a more satisfactory procedure to account for the anharmonic component of the Debye–Waller factor and introducing a number of constraints to reduce the total number of variable parameters. This had led to a marked improvement in the agreement between calculated and observed intensities and to a corresponding reduction in the estimated standard deviations of the occupation numbers of the three types of oxygen atom. As a result of the new analysis, we can now conclude that the most likely configuration for the defect complex in $\text{UO}_{2.12}$ is the so-called 2:2:2 configuration, to be described below.

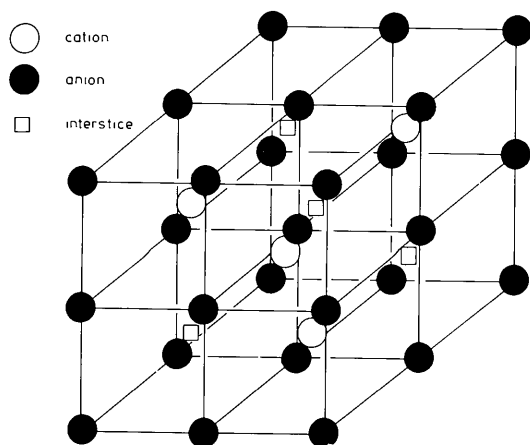


Fig. 1. Unit cell of UO_2 showing the cubic-coordinated cation sites, the tetrahedrally coordinated anion sites, and the cubic-coordinated interstitial sites.

2. Results from earlier analysis

Table 1 summarizes the results from the earlier analysis of Willis (1964). For convenience in comparing with § 3, the results are presented in a slightly different form from the earlier table.

The quantities in parentheses in Table 1 represent standard deviations, as estimated in the least-squares analysis of observed and calculated structure factors from the inversion of the least-squares matrix. The 12 variables (including overall scale factor) were determined from 38 independent structure factors. The R factor is a measure of the disagreement between observed (F_{obs}) and calculated (F_{calc}) structure factors and is defined by

$$R = (\sum |F_{\text{obs}}| - \sum |F_{\text{calc}}|) / \sum |F_{\text{obs}}|$$

where the summations are over the 38 reflections.

With the uranium atom at the origin of the average cell, the undisplaced or 'lattice' oxygens are at $(\frac{1}{4} + u, \frac{1}{4} + u, \frac{1}{4} + u)$. For the fluorite structure the lattice oxygens occupy the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ sites, but a significant reduction in the R factor was achieved by allowing a small displacement, defined by the refinable parameter u , along the four tetrahedral directions $\langle 111 \rangle$. In effect, each oxygen atom is replaced by four quarter-oxygens displaced slightly along the tetrahedral directions. The quarter-oxygens are allowed isotropic Debye-Waller factors in the least-squares analysis. The displacement parameter u is a device for treating the anharmonic, anisotropic component of the Debye-Waller factor. Because of the high temperature, 800°C, required for the experiment, this anisotropic component is quite appreciable. A more satisfactory treatment of anharmonicity is to place the oxygen atom at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position and to allow it to vibrate anharmonically about this equilibrium position: this is the method adopted in the new analysis described in § 3.

The cubic-coordinated interstitial site is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The average cell belongs to the space group $Fm\bar{3}m$, and the interstitial oxygen O' in Table 1 is displaced along any of the twelve $\langle 110 \rangle$ directions from $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the interstitial oxygen O'' is displaced from the same position along any of the eight $\langle 111 \rangle$ directions.

The 'composition number' in the third column of Table 1 is derived from the site occupation numbers of

the different atoms in the average cell and gives the quantities a, b, c, d in the formula unit $U_a O_b O'_c O''_d$. The quantity a is within one standard deviation of unity: this means that the oxygen defects are incorporated in the fluorite structure without causing any defects to appear in the uranium sublattice. An obvious constraint is that $b + c + d = 2.12$, and this constraint has been included in the analysis of § 3. The quantities $c (=0.08)$ and $d (=0.16)$ have standard deviations which are too high to allow any definite choice to be made between the various models that have been proposed for the defect structure of UO_{2+x} .

The last column of Table 1 gives the root-mean-square displacement of the atom from its equilibrium position. In the least-squares analysis this displacement was treated as an isotropic Debye-Waller factor, but it possesses both a thermal component and a static component arising from lattice strain around the individual atoms. The standard deviations of the r.m.s. displacements for the O' and O'' interstitial atoms are so high that there is no reason to believe that the three types of oxygen atom have different displacements. For this reason all three displacements are constrained to be the same in the analysis of § 3.

3. Results from new analysis

The most important anharmonic component of the Debye-Waller factor arises from the anisotropic motion of the tetrahedrally coordinated lattice oxygens. This anisotropy is such that the lattice oxygen spends more of its time along the four $\langle 111 \rangle$ directions directed away from its nearest neighbours than along the four $\langle 111 \rangle$ directions towards the nearest uraniums. In the new analysis the anharmonic contribution to the Debye-Waller factor was allowed for by considering each lattice oxygen to vibrate independently in its own effective one-particle potential of tetrahedral symmetry $\bar{4}3m$. [For a general treatment of this approach see Willis & Pryor (1975).] The one-particle potential may be written

$$V(xyz) = V_0 + \frac{1}{2} \alpha (x^2 + y^2 + z^2) + \beta xyz,$$

where the displacement along the xyz axes has a harmonic component whose magnitude is determined

Table 1. Defect structure of $UO_{2.12}$ (Willis, 1964)

Atom	Atomic coordinates in average cell	Composition number	R.m.s. displacement (Å)
Uranium	0 0 0	1.00 (0.01)	0.12 (0.02)
Lattice oxygen O	$\frac{1}{4} + u, \frac{1}{4} + u, \frac{1}{4} + u$	1.87 (0.03)	0.14 (0.02)
Interstitial oxygen O'	$\frac{1}{2} + v, \frac{1}{2} + v, \frac{1}{2} + v$	0.08 (0.04)	0.15 (0.13)
Interstitial oxygen O''	$\frac{1}{2} + w, \frac{1}{2} + w, \frac{1}{2} + w$	0.16 (0.06)	0.16 (0.14)

$u = 0.017$ (0.001); $v = 0.12$ (0.01); $w = 0.09$ (0.01).
Space group = $Fm\bar{3}m$. R factor = 3.5%.

Table 2. *Defect structure of* $\text{UO}_{2.12}$: *new analysis*

Atom	Atomic coordinates	Composition number
Uranium	0 0 0	1.00 (0.01)
Lattice oxygen O	$\frac{1}{4} \frac{1}{4} \frac{1}{4}$	1.87*
Interstitial oxygen O'	$\frac{1}{2} \frac{1}{2} + v \frac{1}{2} + v$	0.13 (0.02)
Interstitial oxygen O''	$\frac{1}{2} + w \frac{1}{2} + w \frac{1}{2} + w$	0.12 (0.02)

$$v = 0.11 (0.01), w = 0.11 (0.01), R = 2.3\%.$$

* Constrained to give correct composition.

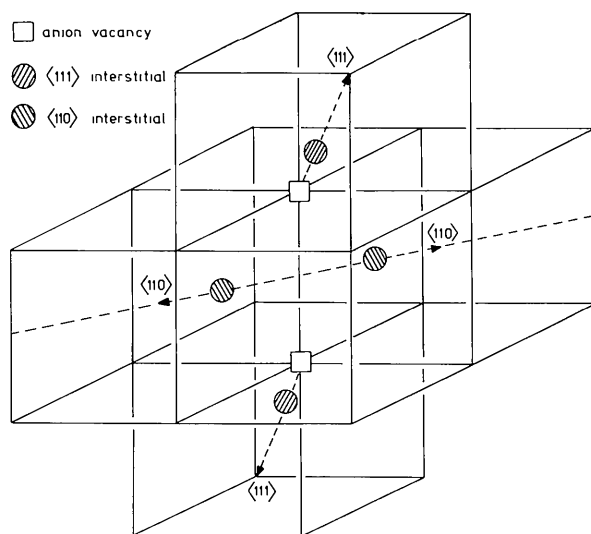


Fig. 2. 2:2:2 cluster. The corners of the cubes indicate the positions of the undisplaced anion sites. The cluster contains two anion vacancies, two $\langle 111 \rangle$ interstitial oxygens, and two $\langle 110 \rangle$ interstitial oxygens.

by the coefficient α and an anharmonic component with magnitude determined by β . It was assumed that the vibrations of the interstitial oxygens, O' and O'', were harmonic and determined by the same value of α as for the lattice oxygens. Altogether three variable parameters were used to describe the thermal vibrations of the atoms: an α value for uranium, an α value for the three types of oxygen atom and a β value for the lattice oxygens.

The total number of adjustable parameters in the new analysis was nine, including the overall scale factor. This compares with twelve parameters for the unconstrained refinement of § 2. The atomic coordinates and composition numbers yielded by the new analysis are summarized in Table 2.

Comparing Tables 1 and 2, we see that Table 2 gives a lower R factor and an appreciably reduced estimated standard deviation for the compositions of the interstitial atoms. The composition numbers of O' and O'' and of the vacant lattice oxygens O in the final column of Table 2 are equal within one standard deviation and are compatible with the composition numbers for the 2:2:2 defect complex, which contains two O' interstitial atoms, two O'' interstitial atoms and two vacancies in the lattice oxygen sublattice. This complex is illustrated in the drawing in Fig. 2.

References

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