The Accommodation of Oxygen Clusters in Hyperstoicheiometric Uranium Dioxide and Its Effects on Crystal Structure

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Hyperstoicheiometric UO_2 is described in terms of chains of oxygen defect clusters parallel to the ⟨110⟩ direction within the parent fluorite lattice. The propagation of such cluster chains in more than one ⟨110⟩ direction is considered and the crystallographic properties of 4 : 3 : 2 clusters used to allow 2 : 2 : 2 cluster chains to cross. The compositional range over which interstitial clusters may be accommodated is assessed and the large tolerance of non-stoicheiometry in the fluorite lattice used to rationalise the overall structures in the uranium–oxygen system from UO_2 to UO_3.

The broad range of non-stoicheiometric phases which exists in UO_2 may be generally attributed to its variable cation valency. In hyperstoicheiometric oxides U^{4+} is readily oxidised to U^{5+} and U^{6+} with charge compensation achieved by the incorporation of oxygen interstitials. In UO_{2+x}, for deviations from stoicheiometry not exceeding $x = 0.10$, particularly at high temperatures, these interstitial defects may be treated as though they were distributed randomly. However, for larger deviations from stoicheiometry the oxygen interstitials interact and, under Coulombic forces, may cluster around the oxidised uranium ion.

Evidence of cluster formation has been provided by a combination of neutron diffraction experiments and computer simulation calculations. From the neutron diffraction experiments of Willis [1-3] on $UO_{2.12}$ an interstitial cluster known as the ' 2 : 2 : 2 cluster ' was proposed. The stability of this and other clusters was investigated by Catlow [4,5] and Catlow and Lidiard [6] using modern computational methods to calculate the energetics and structures of defect aggregates. The 2 : 2 : 2 clusters were shown to be stable for $UO_{2.12}$ but for U_4O_9, Catlow [4] argued that a more realistic and stable cluster may be identified as the 4 : 3 : 2 type. Even larger clusters or ' multiclusters ' based on an aggregate of six 4 : 3 : 2 clusters have been proposed by Cheetham *et al.*[7] for CaF_2 which has an analogous fluorite structure containing excess anions.

An alternative to the multicluster approach has been proposed by Allen *et al.* [8] for the defect structure of U_4O_9. The interpretation of *X*-ray photoelectron spectra [9] in terms of a modified oxygen co-ordination was the basis for postulating a change in co-ordination from eight to ten for uranium atoms bridging two 2 : 2 : 2 clusters. Thus the systematic linear ordering of cluster chains parallel to ⟨110⟩ was proposed [10] to account for the ordering observed in the transition from the disordered structure of UO_{2+x} to the superlattice structure of U_4O_9.

In this paper the systematic linear ordering of 2 : 2 : 2 clusters will be examined in detail. In addition, the propagation of cluster chains in more than one ⟨110⟩ direction will be considered and the crystallographic properties of 4 : 3 : 2 clusters will be used to allow 2 : 2 : 2 cluster chains to cross. Moreover, a larger composition range over which interstitial clusters may be accommodated in the UO_2 fluorite structure will be assessed in the light of observations of distorted cubic structures in U_3O_7 [11] and U_2O_5.[12] This larger tolerance of non-stoicheiometry by the fluorite structure is argued as justification for a re-classification of the overall structures prevailing in the oxide range UO_2—U_3O_8—UO_3.

Results

Ordering of 2 : 2 : 2 *Clusters.*—The 2 : 2 : 2 cluster identified by Willis [1-3] contains two oxygen interstitial atoms along ⟨110⟩ identified as O′, two oxygen interstitial atoms along ⟨111⟩ identified as O″, and two vacancies in the oxygen sublattice. For low values of x in UO_{2+x} a random distribution of clusters is envisaged. For higher values of x however, Allen and Tempest [10] argued that under Coulombic forces, the clusters would order and a superstructure would develop. The extra reflections in neutron diffraction patterns of U_4O_9 are clear evidence of additional atomic ordering in a superlattice and it was postulated that the ordering of 2 : 2 : 2 clusters occurred in ⟨110⟩ directions.

Figure 1 illustrates a chain of 2 : 2 : 2 clusters along ⟨110⟩ within which each uranium atom has the co-ordination number ten. Using the most recent neutron diffraction data [3] to calculate interatomic distances, we find that there are four normal U–O bonds of 2.37 Å, four U–O′ of 2.22 Å, and two U–O″ of 2.30 Å in the chain direction. The reduction of *ca.* 5% in the uranium–oxygen interstitial bond length compared to that existing for normal U–O bonds in the undistorted regions of the fluorite lattice emphasises the increased covalent nature of the bonding within the chain.

The degree of non-stoicheiometry in the UO_2 fluorite lattice depends on its ability to incorporate 2 : 2 : 2 clusters and chains of ordered clusters. The crystallographic properties of the chains place restrictions on the capacity of the cubic structure to accommodate increasing amounts of oxygen. For instance, to minimise the interaction between neighbouring O″ atoms continuous parallel chains are only allowed in every alternate uranium layer parallel to ⟨001⟩. Otherwise O′ and O″ atoms would occupy the same empty cube in the sublattice, an extremely unlikely event judged from considerations of ionic radii and the separation of the interstitial sites as measured by Willis.[3] In the ⟨110⟩ direction, however, there is less restriction on chain spacing and Figure 2 shows that a minimum spacing of $\sqrt{2}a_0$ (where a_0 is the lattice parameter of the parent UO_2 fluorite lattice) can be tolerated. Again to avoid interference between O″ ions, chains with the same x,y co-ordinates must have z values of 0, $\frac{1}{2}$ or $\frac{1}{4}$, $\frac{3}{4}$ when related to a unit cell of edge $4a_0$. Since the number of additional oxygens incorporated by the lattice is simply the number of O′ interstitials (in a 2 : 2 : 2 cluster the number of O″ interstitials equals the number of vacancies), it can be seen from Figure 2 that, within a unit cell of edge $4a_0$ containing 512 oxygen atoms, there are an additional 128 O′ interstitials giving an

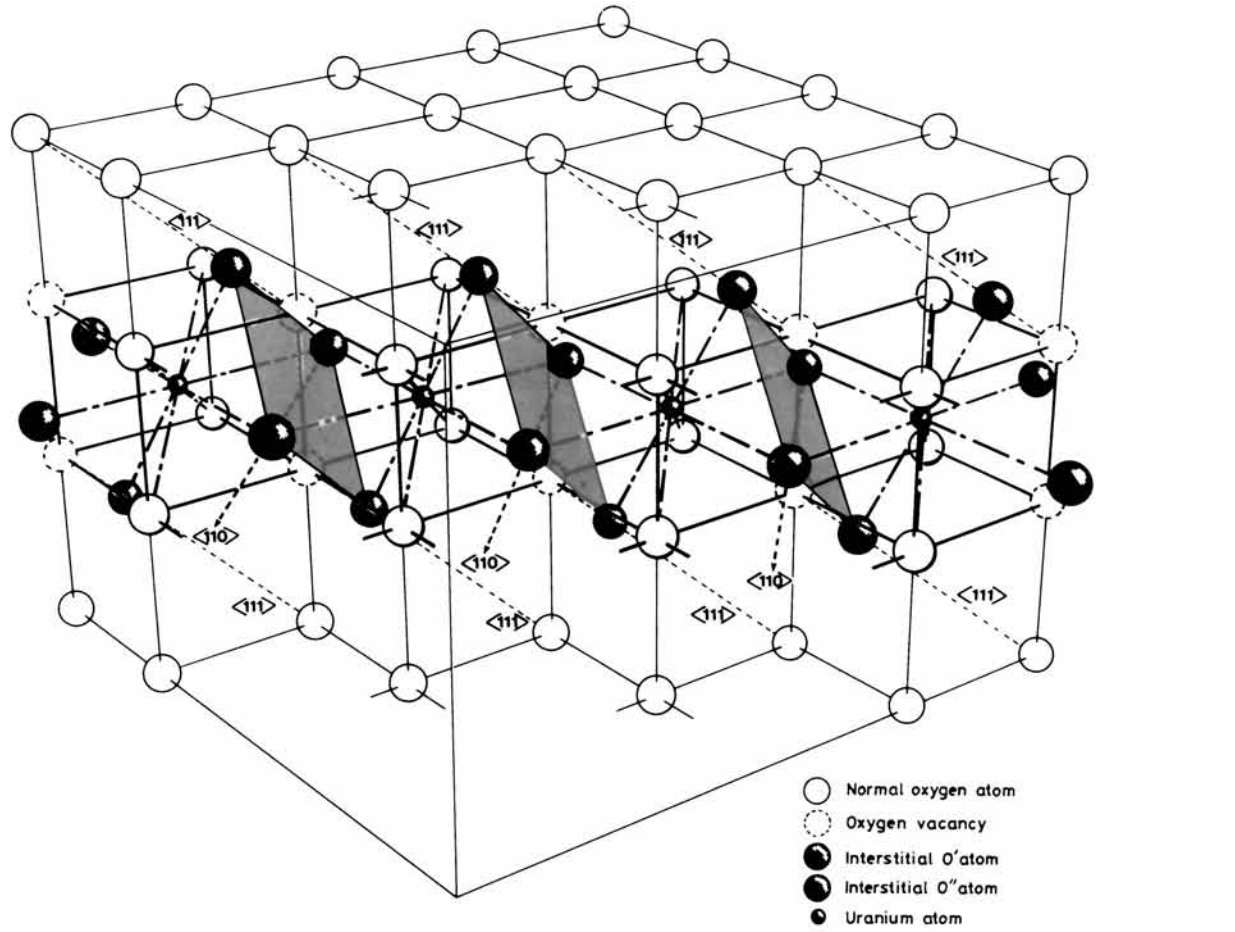

Figure 1. A chain of 2 : 2 : 2 clusters in the oxygen sublattice of UO_2

oxide composition of U_2O_5. An increase in the distance of closest approach in the ⟨110⟩ direction to $2\sqrt{2}a_0$ yields the composition U_4O_9 and intermediate compositions between U_4O_9 and U_2O_5 can easily be accommodated.

It is clear that the composition of hyperstoicheiometric oxides up to U_2O_5 can be achieved by the incorporation of oxygen interstitials in chains of 2 : 2 : 2 clusters parallel to ⟨110⟩. However, from neutron diffraction data it appears that interstitial sites in all six directions of the ⟨110⟩ family are possible. Furthermore, it is known that the space group of U_4O_9 is $I\bar{4}3d$ [13] and a unique chain direction does not possess the symmetry necessary to satisfy this space group. Consequently chains must be parallel to more than one ⟨110⟩ direction and in all probability meet at certain points.

The 4 : 3 : 2 *Cluster and Chain Crossing.*—The structures of defect aggregates in UO_{2+x} have been calculated by Catlow [5] using computational methods to minimize the crystal energy with respect to atomic co-ordinates. Although the general procedure is ideally suited to fully ionic crystals, stable defect clusters were reported for UO_{2+x} and U_4O_9 even though the nature of the bonding is less certain. Successive cluster stages which occur as the defect concentration is raised were examined, and for $UO_{2.12}$, the 2 : 2 : 2 cluster was shown to be a very stable arrangement. However, for U_4O_9, the results indicated that the complex distribution of interstitials could reduce to an ordered arrangement of 4 : 3 : 2 clusters. A 4 : 3 : 2 cluster is shown in Figure 3. It contains four oxygen interstitials along ⟨110⟩, three oxygen vacancies and two interstitials along ⟨111⟩. Interestingly it should be noted that the displacements of the O′ interstitials from the oxygen cube centres for both 2 : 2 : 2 and 4 : 3 : 2 clusters as calculated by Catlow [5] were only *ca.* 0.2 Å, much less than the observed value of *ca.* 0.85 Å from neutron diffraction data.[2]

A noteworthy feature of the 4 : 3 : 2 cluster is the orthogonal relationship between the O″ interstitials displaced along ⟨111⟩, although the ⟨111⟩ displacements themselves are not orthogonal. This property contrasts with the parallel relationship in a 2 : 2 : 2 cluster and suggests a construction whereby two orthogonal 2 : 2 : 2 cluster chains could cross with minimal lattice distortion. Such an arrangement is shown in Figure 4. With this chain formation the incompatibility of symmetry requirements from the $I\bar{4}3d$ space group and a unique chain axis is partly removed, and is completely removed if the three allowed equivalent ⟨110⟩ crossed chains are taken into consideration. Thus, this one property of the 4 : 3 : 2 cluster with respect to chains crossing brings together Catlow's suggestions that 4 : 3 : 2 clusters are basic units in highly oxidised uranium and those of Allen and Tempest [10] who believe that linearly ordered 2 : 2 : 2 clusters are also present.

The exact atomic co-ordinates of the O′ interstitials present in a 4 : 3 : 2 cluster when it bridges two cluster chains have yet to be determined. An important factor in any calculation of this type is the dual role which these particular O′ interstitials now assume. At the chain crossover point both O′ interstitials in one chain act as though they are O″ interstitials in the other chain. Thus all four O′ interstitials parallel to ⟨110⟩ in a

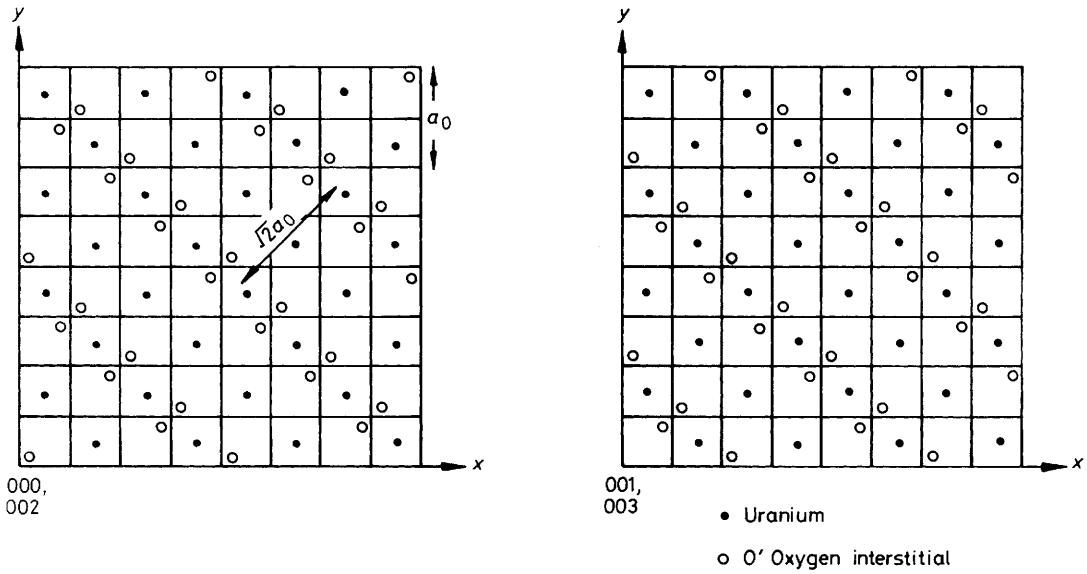

Figure 2. An arrangement of ordered 2 : 2 : 2 cluster chains in the UO_2 fluorite lattice yielding the composition U_2O_5 (normal oxygen and O″ interstitial atoms not shown)

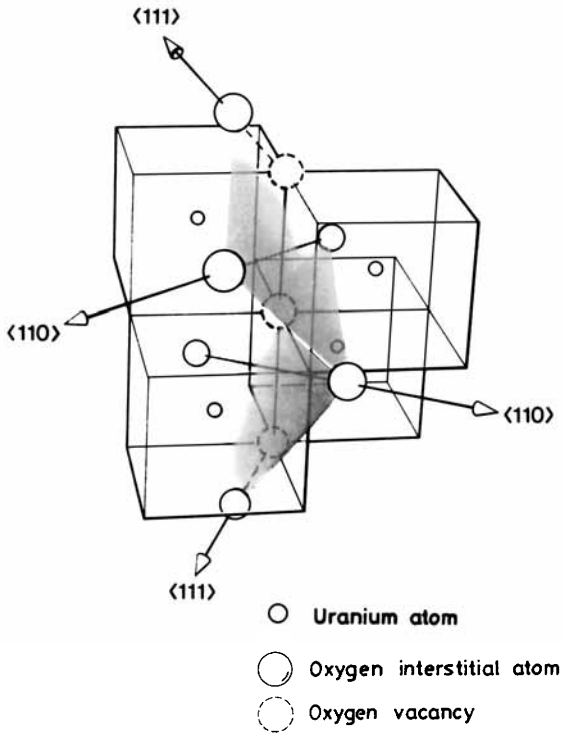

Figure 3. The oxygen sublattice showing a 4 : 3 : 2 cluster

4 : 3 : 2 cluster must move to a compromise position partially to satisfy the requirements of displaced O″ interstitials in the adjoining 2 : 2 : 2 clusters. These positions will be close to the empty oxygen cube centres in agreement with the calculations of Catlow which showed that the distortion along <110> from the centres was only *ca.* 0.1 Å. These displacements were probably masked by 2 : 2 : 2 cluster distortions in $UO_{2.12}$ and are not at variance with the larger displacements found by Willis.[2]

Cluster Formation in the U_4O_9—U_2O_5 *Range.*—The increased electrostatic force between uranium atoms separated by a 2 : 2 : 2 cluster produces a lattice shrinkage along a unique [110] chain axis. Conversely, O′ interstitials along [1$\bar{1}$0] produce a lattice expansion. Hence in U_4O_9 and U_3O_7 the presence of preferentially oriented chains will distort the lattice from cubic symmetry. Significant distortion from the cubic to the rhombohedral structure in the superlattice of U_4O_9 has in fact been observed.[14] The U_3O_7 composition can also be accommodated by suitably spaced 2 : 2 : 2 cluster chains in the fluorite lattice but, as yet, no complete experimental determination of its crystal structure exists. Two modifications, α-U_3O_7 and β-U_3O_7, have been reported.[15–17] The diffraction patterns of both forms have been indexed on the basis of tetragonal unit cells approximately isodimensional with that of UO_2 [11] although it is possible that the true unit cells are superlattices similar to that of U_4O_9 but perhaps with lower symmetry. The α modification of U_3O_7 has a unit-cell parameter ratio $c : a \simeq 0.99 : 1$, whilst β-U_3O_7 has $c : a \simeq 1.03 : 1$. Such distortions are possible with preferentially ordered cluster chains.

It was shown earlier that the limiting composition for a fluorite lattice containing pure 2 : 2 : 2 cluster chains was U_2O_5. Although, the only reported crystal structure of U_2O_5 at normal temperatures and pressures has been the orthorhombic classification of Rundle *et al.*,[18] Hoekstra *et al.*[12] have identified a stable monoclinic phase above 1 073 K and 60 kbar (6×10^9 Pa). The cell constants $a_0 = 5.41$, $b_0 = 5.48$, $c_0 = 5.41$ Å, and $\beta = 90.49°$ represent a contracted and distorted UO_2 fluorite lattice in which normally $a_0 = 5.47$ Å. The difficulty in forming a fluorite lattice with composition U_2O_5 is not really surprising if the probability of 2 : 2 : 2 chain interaction and 4 : 3 : 2 cluster formation is considered. In terms of composition only, if each pair of 2 : 2 : 2 clusters could be replaced by a 4 : 3 : 2 cluster (a 4 : 3 : 2 cluster can be pictured as two 2 : 2 : 2 clusters at right angles) then the maximum U_2O_5 composition would be reduced to $UO_{2.375}$ (U_8O_{19}). This decrease occurs because the four O′ interstitials in a 4 : 3 : 2 cluster are tetrahedrally arranged around an extra oxygen vacancy so that the number of additional oxygen atoms which can be incorporated is reduced by a quarter from U_2O_5 to $U_2O_{4.75}$.

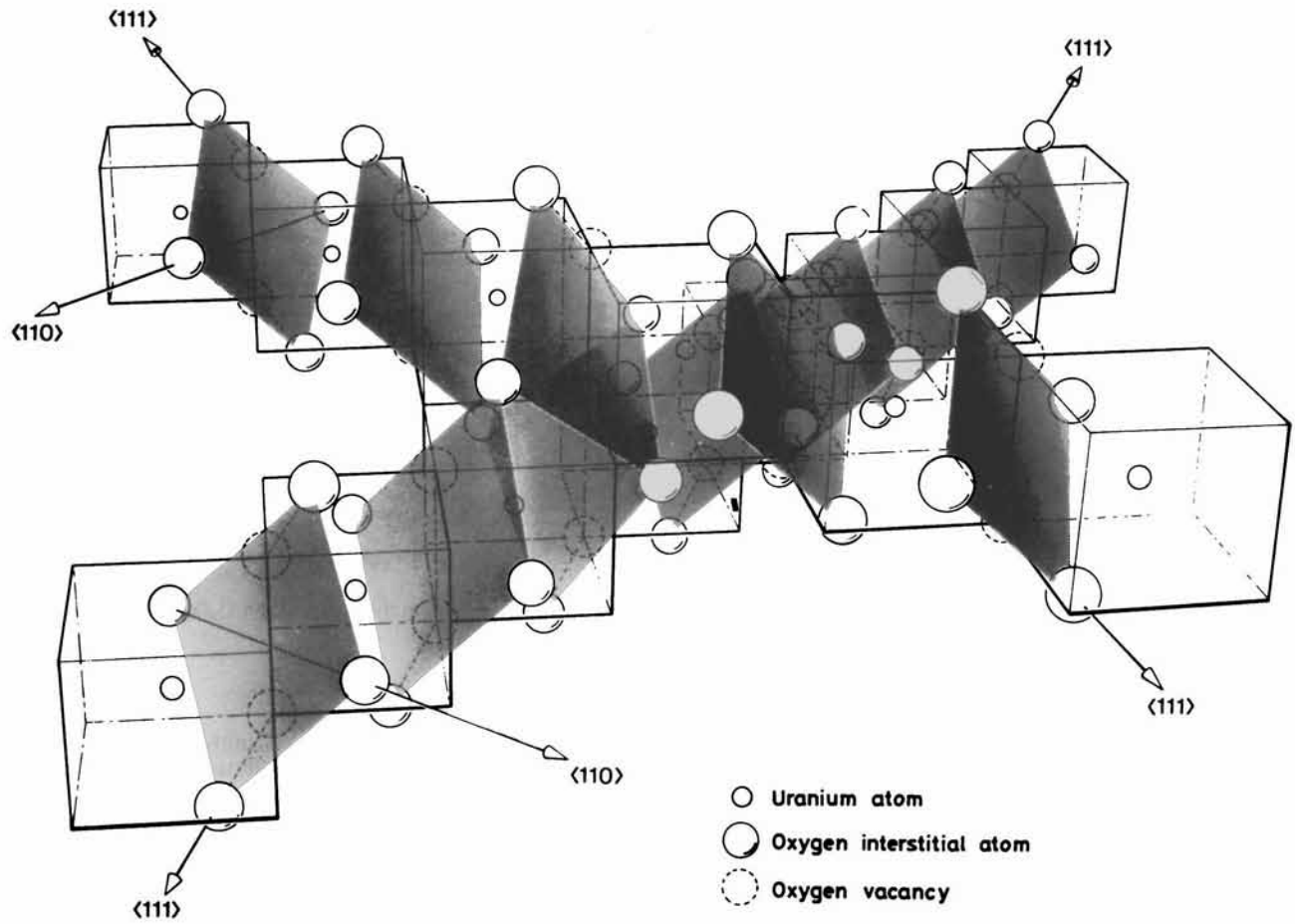

Figure 4. The crossing of orthogonal 2 : 2 : 2 cluster chains at a 4 : 3 : 2 cluster

Discussion

It is unlikely in practice to find ideally distorted fluorite structures with either 2 : 2 : 2 cluster chains or 4 : 3 : 2 clusters exclusively. Oxygen migration and condensation at stable sites can occur by several energetically similar mechanisms. Consequently, mixtures of 4 : 3 : 2 clusters and 2 : 2 : 2 cluster chains are to be expected, with a greater number of 4 : 3 : 2 clusters present in the more highly oxidised crystals. This picture fits the experimental evidence very well. Several intermediate phases with complex structures based on a distorted fluorite structure have been identified in the oxide range U_4O_9—U_2O_5. The occurrence of any one particular structure in preference to another one is largely due to the changes in defect formation and migration energies caused by different temperatures and oxygen partial pressures. Nevertheless, the link between distorted fluorite UO_2 and oxides up to U_2O_5 should not be ignored simply because the distortion changes the crystal symmetry from cubic to tetragonal, rhombohedral, or even monoclinic. More importantly, the uranium–oxygen chemical bonding and co-ordination numbers are not dramatically affected. Thus a phase change from, for example, cubic U_4O_9 to tetragonal U_3O_7 need not be associated with gross differences in the physical properties of the two phases, since the phase changes occur because of the regrouping of ordered 2 : 2 : 2 cluster chains and 4 : 3 : 2 clusters. It is the local effect of the defect configurations rather than the overall symmetry which has the greater effect on material properties. Only for new phases based on significantly different U–O bond lengths and co-ordination numbers such as the seven-co-ordinate uranium in oxygen pentagonal bipyramids of the U_3O_8 structure, would a large change in properties be expected. Of course with such a large change in the local uranium–oxygen environment and the disappearance of oxygen clusters the distorted fluorite structure is destroyed completely and is replaced by another stable structure. Indeed the orthorhombic structure of α-U_3O_8 may be assumed to be one with equivalent stability to that of fluorite UO_2. According to Loopstra [19] all uranium atoms are in a similar co-ordination environment and the oxygen pentagonal bipyramids share edges and corners to form an infinite sheet. This layer-like structure is essentially the same for all the compounds in the range U_2O_5—UO_3 with a whole range of superstructures represented by the formula U_3O_{8-y}.

From this recognition of the stability of the UO_2 and U_3O_8 structures a simplified assessment of the UO_2—U_3O_8 phase diagram can be made. Figure 5 shows the major phases commonly encountered with a metastable range between U_3O_7 and U_2O_5, when neither pure distorted hyperstoicheiometric UO_2 nor pure distorted hypostoicheiometric U_3O_8 are easily formed. In fact, because of their stability the likelihood is that both these phases (the γ phase or U_4O_{9+x}, and U_3O_{8-y}) coexist at equilibrium without any intermediate U_2O_5 phase being formed.

The hatched pattern to the left and right hand side of Figure 5 is used to indicate the characterised range of stoicheiometry for both the fluorite and orthorhombic structures. For the range of composition UO_2—U_4O_9 the fluorite structure is, of course, well known and needs no further discussion but the range U_3O_{8-z}—UO_3 may be described using α-UO_3

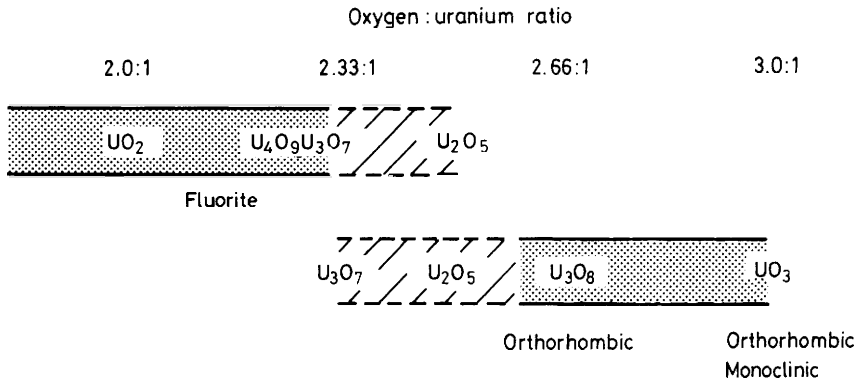

Figure 5. Structural relationship of uranium oxides

as the basic structure type simply related to other well known structures.[20] In this case α-U_3O_8 may then be viewed as oxygen-deficient α-UO_3 with ordered oxygen vacancies. More recently though, Greaves and Fender [21] have suggested an alternative approach preferring to regard the α-UO_3 structure as uranium-deficient α-U_3O_8 with uranium vacancies introduced so as to re-establish an O : U stoicheiometry of 3 : 1. Either way the close relationship between these two orthorhombic structures is established and they have therefore been associated in Figure 5.

The literature dealing with structural aspects of the uranium–oxygen system is extensive. More than 30 phases have been described but about 70% of these are to be found towards the centre of the compositional range $UO_{2.00} \longrightarrow UO_{3.00}$ where the two dominant structures transform. The cubic structure has been characterised throughout the entire range of composition considered here from the simple fluorite structure of UO_2 to a reportedly dark red cubic form of UO_3 prepared [22] by the ignition of β-$UO_3 \cdot H_2O$ for 24 h in air at 375 °C. For the higher oxygen contents though, the orthorhombic structure predominates and it is between the characteristic UO_2 and α-UO_3-type structures that a variety of tetragonal, hexagonal, and monoclinic phases have been identified; some of the latter being stable only at elevated temperature or pressure.

Acknowledgements

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Received 3rd *May* 1983; *Paper* 3/697