Linear Ordering of Oxygen Clusters in Hyperstoicheiometric Uranium Dioxide

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The formation of hyperstoicheiometric oxides of UO_2 by the incorporation of additional oxygen atoms in the parent fluorite structure is described in terms of 2 : 2 : 2 oxygen clusters. A 2 : 2 : 2 cluster between two uranium atoms is treated as a co-ordination defect and consideration of electrostatic and polarisation effects together with *X*-ray photoelectron spectral data suggests that defect ordering is likely along ⟨110⟩ directions. The effect of chain-like linear ordering of oxygen clusters on structures in the oxide system UO_2–U_3O_8 is assessed and a crystal structure for U_4O_9 is postulated.

Oxygen can be readily transferred between the fluorite-type structure of UO_2 and the ambient gas phase. Stoicheiometric UO_2 is not easy to obtain and a series of oxidation products can be formed at different temperatures (see Figure 1). In the fuel cycle of many nuclear reactors UO_2 is subject to a wide range of temperatures. At full power temperatures as high as 2 000 K are envisaged at the centre of the fuel rods and thermal cycles between these high temperatures and room temperature are not uncommon.

Above 1 300 K, a homogeneous hyperstoicheiometric UO_{2+x} phase exists between UO_2 and $UO_{2.2}$ depending on the oxygen potential of the surroundings. However, during thermal cycling to room temperature the extremely rapid self-diffusion of oxygen [1] could cause the system to become diphasic with the formation of a second ordered U_4O_{9-y} phase, particularly in a failed fuel rod where there is direct gas access to the UO_2. During the proposed dry storage of UO_2 fuel rods, the effects of temperatures up to 500 K and high oxygen potentials must be considered. After removal from the reactor the fuel consists of UO_2 with small amounts of UO_{2+x}, although precipitates of higher oxides have been observed in failed fuel rods.[2] The concentrations of these phases would be expected to change with storage time and the transformation of the parent fluorite structure of UO_{2+x} and U_4O_{9-y} to α-U_3O_7 and β-U_3O_7, or even U_3O_8 eventually, could limit the long-term stability of stored fuel.

The formation of UO_{2+x} and U_4O_9 occurs by the incorporation of additional oxygen atoms at interstitial sites in the fluorite structure of UO_2, rather than the creation of uranium vacancies, and the occupation number of cations remains the same as in the stoicheiometric compound. The thermodynamic stability and physical properties of UO_2 compounds containing excess oxygen depends on the available interstitial sites and the degree of occupancy of oxygen at these sites. In UO_{2+x} two types of interstitial site have been identified by Willis [3,4] from neutron diffraction data. Although it is likely that the interstitial oxygen atoms also form clusters in U_4O_9 the exact co-ordinate position of all 64 interstitial atoms in the unit cell has not been established. However, a model has been proposed by Belbeoch *et al.*[5] based on the $I\bar{4}3d$ space group indicated by single-crystal *X*-ray diffraction data in which the extra oxygens are distributed very heterogeneously.

An alternative distribution of interstitial oxygen clusters in U_4O_9 has been put forward by Allen *et al.*[6] Satellite structure observed in the uranium 4*f* *X*-ray photoelectron spectrum of UO_{2+x} was interpreted in terms of a modified oxygen co-ordination and this, in turn, was the basis for postulating a change in co-ordination from eight to ten for uranium atoms bridging two 2 : 2 : 2 oxygen clusters. Cluster chains were proposed parallel to ⟨110⟩ 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.

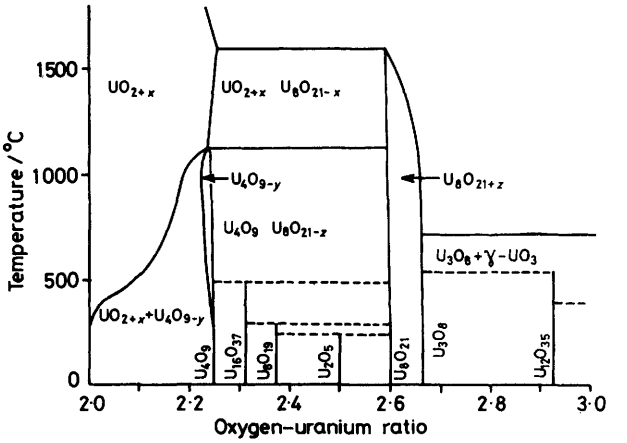

Figure 1. The phase diagram of UO_2–UO_3

In this paper the complete atomic configuration of the unit cell of U_4O_9 is derived using the approach suggested by Allen *et al.*[6] Furthermore, bond length calculations are used to assess the effects of covalency changes in UO_{2+x} and U_4O_9 and the consequent effect on physical and chemical properties of hyperstoicheiometric UO_2. Any property changes could affect the performance of UO_2 fuel rods during reactor operation and their stability during dry fuel storage.

Results and Discussion

(*a*) *Defects in* UO_{2+x} *and* U_4O_9.—In fluorite, the parent structure of UO_2, each cation is co-ordinated by a cube of eight anions whilst each structure is co-ordinated by a tetrahedron of four cations. These sites are shown in the unit cell of UO_2 in Figure 2 together with the largest unoccupied cubic-co-ordinated interstitial sites. It has been assumed by some previous workers [5] that the disordered structure of UO_{2+x} consists of the fluorite arrangement with random occupation of the cubic-co-ordinated interstices by oxygen atoms. This view was supported in part by the single-crystal neutron diffraction data of Masaki and Doi.[7] However, according to Willis [3,4] there are two further kinds of interstitial sites which are displaced from the cubic-co-ordinated sites by *ca.* 1 Å in the ⟨110⟩ and ⟨111⟩ directions, and oxygen atoms occupying these sites are identified as O′ and O″ respectively. These displacements do not affect the uranium

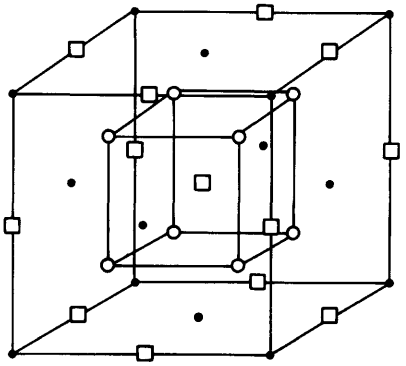

Figure 2. The parent fluorite structure with empty cubic co-ordinated interstitial sites

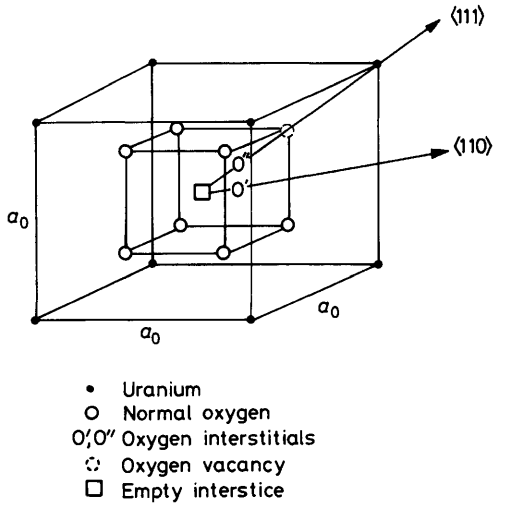

Figure 3. The geometrical relationship between O′ and O″ sites and the empty interstice at the cube centre

sublattice but cause the ejection of some of the normal oxygens from their fluorite positions. The aggregate or ' cluster ' so formed has the so-called 2 : 2 : 2 configuration containing two oxygen vacancies, two O′ atoms, and two O″ atoms.

The formation of clusters contrasts with the structural defects present in other anion fluorite-related superlattices in which the basic oxygen cube of the fluorite structure changes to a square antiprism.[8] However, a detailed analysis of the *X*-ray photoelectron spectrum of UO_{2+x} [9] suggested a defect grouping based on a unique co-ordination of Willis-type clusters in which an individual oxygen atom has a total negative charge less than in the isolated oxygen ion, and an alternative view of the defect fluorite lattice was described by Martin [10] who suggested that ordering of defects could occur to form chains of co-ordination defects. An ordering similar to that suggested by Martin could occur in UO_{2+x} based on Willis-type clusters and, associating these ideas, we derive here a model for the structure of UO_{2+x} including U_4O_9, incorporating a chain-like co-ordination of oxygen defect clusters.

(*b*) *Cluster Ordering and Co-ordination Effects.*—A 2 : 2 : 2 cluster bridges two uranium atoms which then become nine-fold rather than eight-fold co-ordinate. The positions of the interstitial oxygens O′ and O″ and the empty interstice are shown in Figure 3. For the purposes of the calculation of internuclear distances both O′ and O″ are drawn in the same oxygen cube although they are in fact always in separate cubes.

The co-ordinates of the interstitial sites are shown below,

$$\square\ (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$
$$O'\ (\tfrac{1}{2} + v, \tfrac{1}{2} + v, \tfrac{1}{2})$$
$$O''\ (\tfrac{1}{2} + w, \tfrac{1}{2} + w, \tfrac{1}{2} + w)$$

where $v = 0.12$ and $w = 0.09$ according to Willis [3] or both are equal to 0.11 according to a revised assessment of neutron diffraction data.[4]

The displacements of O′ and O″ from the empty site □ are: $\square - O' = v\sqrt{2}a_0 = 0.851$ Å and $\square - O'' = w\sqrt{3}a_0 = 1.042$ Å, where $a_0 = 5.47$ Å.

Taking a_0 to be 5.47 Å for stoicheiometric UO_2, and using the above values for the distance of oxygen interstitials from the oxygen cube centre, interatomic distances can be calculated by simple trigonometry and the results are shown in the Table. Using the most recent data [4] we have six U–O at 2.37, two U–O′ at 2.22, and one U–O″ at 2.30 Å emphasising the higher degree of covalency in the uranium–cluster bonds. Calculations based on more recent results have eliminated some of the irregularities in Willis's early data,[3,11] particularly noticeable being the increase of the previously rather short O′–O′ distance of 2.01 Å to 2.17 Å. Calculations were also made using estimated data and these indicated quite clearly that small changes in the parameters *v* and *w* introduce wide variations specifically in the O′–O′ distance and, although not included in the Table, the O″–O′ distance also. It is noteworthy that the *v* and *w* values used in these calculations are of a magnitude consistent with values derived experimentally by neutron diffraction, and the reason for the very large variation in the O′–O′ and O″–O″ distances so derived may be attributed to the geometrical arrangement of the co-ordination cluster within the UO_2 structure. A change in the O′–O′ distance is directly proportional to *v*, making these distances very sensitive to neutron diffraction data.

These calculations require that the U–U distance be fixed. In practice however this is unlikely to be so. Single-crystal *X*-ray diffraction studies of defect fluorite-type structures reveal consistent lengthening of U–U and shortening of O–O distances around a vacant oxygen site [12] and similar polarisation effects would be expected in the vicinity of a cluster. In this case the net effect would be a shortening of the U–U interatomic distance across the cluster and the creation of preferred interstitial oxygen sites along the opposite edge of the oxygen cube containing the original defect grouping. Thus in addition to the tendency for clusters to order under coulombic forces to develop a superstructure, on geometrical grounds we can postulate the formation of a 2 : 2 : 2 cluster chain along ⟨110⟩ as shown in Figure 4.

Within the chain each uranium atom has the co-ordination number 10. Most models for the anion excess phase invoke doubly negatively charged interstitials compensated by singly charged holes present as U^{5+} cations.[4] At first sight, bond length data appear to support this view. However, although the average U–O separation in most metal uranate(VI) structures is 2.07—2.10 Å, in the eight-co-ordinate $CaUO_4$ structure, which resembles more closely that considered here, this distance is 2.21 Å (ref. 13) and approaches the values derived above. Measurements of the *X*-ray photoelectron spectra from U_3O_8 in the uranium 4*f* region may also be interpreted in

Table. Internuclear distances (Å) based on a 2 : 2 : 2 cluster

v	w	O–O	U–O	U–O′	U–O″	O–O′	O–O″	O′–O′	O′–O″
0.12 [a]	0.09 [a]	2.74	2.37	2.18	2.35	2.52	2.38	2.01	2.75
0.11 [b]	0.11 [b]	2.74	2.37	2.22	2.30	2.47	2.42	2.17	2.63
0.09	0.11	2.74	2.37	2.30	2.30	2.47	2.42	2.48	2.70
0.09	0.12	2.74	2.37	2.30	2.28	2.54	2.45	2.48	2.62

[a] B. T. M. Willis,[3] 1963. [b] B. T. M. Willis,[4] 1978.

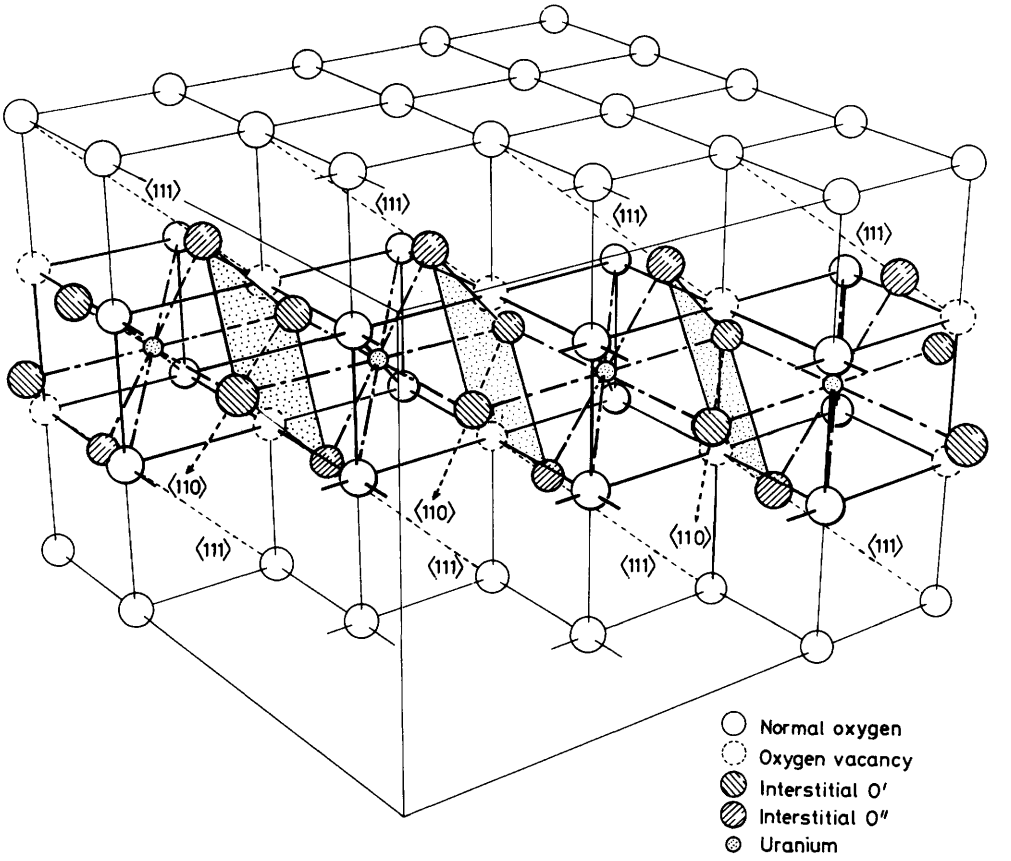

Figure 4. A chain of 2 : 2 : 2 clusters in the oxygen sublattice

terms of a uranium atom in crystallographically inequivalent sites where it apparently resides in 4+ and 6+ ionic configurations [14,15] so that although an interpretation of results from e.s.r measurements on uranates favours the presence of U^{5+} in U^{6+} lattices [16] this may not necessarily be the case in the fluorite structure of UO_2.

(*c*) *Crystal Structure of* UO_{2+x} *and* U_4O_9.—The length and frequency of chains determines the overall nature of the structure. For low values of x in UO_{2+x} a random distribution of clusters is envisaged. As x increases the probability of oxygen interstitials being influenced by clusters already formed increases. Gradually as x approaches 0.25, cluster chains develop and become ordered. Continuous chains are only allowed in every alternative uranium layer parallel to ⟨001⟩ because of O″ interference in the oxygen sublattice. At a distance of closest approach of $2\sqrt{2}a_0$ (where a_0 is the lattice parameter of the parent UO_2 fluorite lattice) in the ⟨110⟩ direction only 32 clusters can be accommodated by a unit cell of edge $4a_0$ which yields the composition of U_4O_9 exactly, and is consistent with the superlattice observed by Willis.[17]

A possible unit cell for U_4O_9 is outlined in Figure 5 where the cubic unit cell of edge $4a_0$ contains six cluster chains and chains (1) and (3) are each shared by two cells. Chains (1), (2), and (3) contain eight clusters whilst chains (4), (5), (6), and (7) contain four each. Since chains along cell faces also contribute interstitial oxygens to other unit cells it can be seen that the complete unit cell contains 64 O′ interstitials, 64 O″ interstitials, and 64 vacancies, making a total of 64 additional oxygen atoms. Thus the proposed unit cell of U_4O_9 contains 64 unit cells of UO_2 with 256 uranium atoms, 448 oxygen atoms on 'normal' sites plus 128 additional interstitial O′ and O″ oxygens. Assuming that a uranium atom is positioned at the origin (0,0,0) the co-ordinates of O′ and O″ are shown below.

(*i*) O′ *Interstitials*. There are 48 O′ atoms at (0,0,0; 0,0,½; ½,0,¼; 0,½,¼; ½,0,¾; 0,½,¾) + v,⅛ − v,0; ⅛ − v,v,0; ⅛ + v,¼ − v,0; ¼ − v,⅛ + v,0; ¼ + v,⅜ − v,0; ⅜ − v,¼ + v,0; ⅜ + v,½ − v,0; ½ − v,⅜ + v,0; and 16 more at (0,0,0; 0,0,½) + ½ + v,⅝ − v,0; ⅝ − v,½ + v,0; ⅝ + v,¾ − v,0; ¾ − v,⅝ + v,0; ¾ + v,⅞ − v,0; ⅞ − v,¾ + v,0; ⅞ + v,1 − v,0; 1 − v,⅞ + v,0.

(*ii*) O″ *Interstitials*. There are 32 O″ atoms at (½,0,¼; 0,½,¼; ½,0,¾; 0,½,¾) + w,w,⅛ − w; ⅛ − w,⅛ − w,w − ⅛; ⅛ + w,⅛ + w,⅛ − w; ¼ − w,¼ − w,w − ⅛; ¼ + w,¼ + w,⅛ − w;

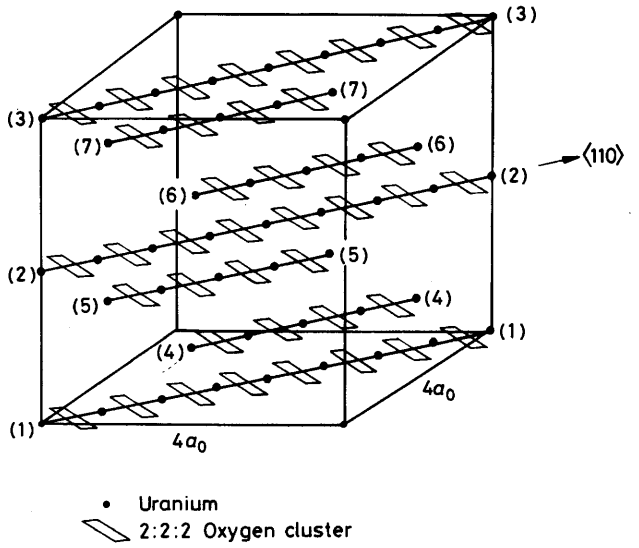

Figure 5. A configuration of seven cluster chains in the unit cell of U_4O_9

$\frac{3}{8} - w,\frac{3}{8} - w,w - \frac{1}{8}$; $\frac{3}{8} + w,\frac{3}{8} + w,\frac{1}{8} - w$; $\frac{1}{2} - w,\frac{1}{2} - w,w - \frac{1}{8}$; 16 more are at (0,0,0; $0,0,\frac{1}{2}$) + $w,w,\frac{1}{8} - w$; $\frac{1}{8} + w,\frac{1}{8} + w,\frac{1}{8} - w$; $\frac{1}{4} + w,\frac{1}{4} + w,\frac{1}{8} - w$; $\frac{3}{8} + w,\frac{3}{8} + w,\frac{1}{8} - w$; $\frac{1}{2} + w,\frac{1}{2} + w,\frac{1}{8} - w$; $\frac{5}{8} + w,\frac{5}{8} + w,\frac{1}{8} - w$; $\frac{3}{4} + w,\frac{3}{4} + w,\frac{1}{8} - w$; $\frac{7}{8} + w,\frac{7}{8} + w,\frac{1}{8} - w$; and a further 16 at (0,0,0; 0,0,1) + $\frac{1}{8} - w,\frac{1}{8} - w,w - \frac{1}{8}$; $\frac{1}{4} - w,\frac{1}{4} - w,w - \frac{1}{8}$; $\frac{3}{8} - w,\frac{3}{8} - w,w - \frac{1}{8}$; $\frac{1}{2} - w,\frac{1}{2} - w,w - \frac{1}{8}$; $\frac{5}{8} - w,\frac{5}{8} - w,w - \frac{1}{8}$; $\frac{3}{4} - w,\frac{3}{4} - w,w - \frac{1}{8}$; $\frac{7}{8} - w,\frac{7}{8} - w,w - \frac{1}{8}$; $1 - w,1 - w,w - \frac{1}{8}$.

The parameters v and w refer to the superlattice unit cell of edge $4a_0$ and are equal to $\frac{1}{4}$ of the atomic co-ordinate parameters determined by Willis [3,4] for O′ and O″ interstitial sites in the UO_2 unit cell of edge a_0 and used in the Table.

In Figure 5 all chains are parallel to the specific [1$\bar{1}$0] direction but chains may run parallel to all directions in the ⟨110⟩ family without crossing in any one (a,b) plane. Nevertheless the chain spacing remains at $a_0/2$ (~11 Å) in the c direction and $\sqrt{2}/2a_0$ (~15.5 Å) in any (a,b) plane.

(*d*) *Higher Hyperstoicheiometric Phases of* UO_2.—A chain spacing of $\frac{3}{2}\sqrt{2}a_0$ parallel to ⟨110⟩ yields U_3O_7 but is not consistent with the U_4O_9 superlattice. Any increase in oxygen content above U_3O_7 would involve severe distortion of the parent fluorite lattice since additional oxygen atoms would have to be accommodated by oxygen cubes already distorted by O′ or O″ interstitials. Thus the increased electrostatic force between uranium atoms separated by a 2 : 2 : 2 cluster produces a lattice shrinkage along the unique [1$\bar{1}$0] chain axis. Conversely, O′ interstitials along [110] produce a lattice expansion. Hence in U_4O_9 and U_3O_7 the presence of one or several preferentially oriented chains will distort the superlattice from cubic symmetry. Significant distortion from the cubic to rhombohedral structure in the superlattice of U_4O_9 has in fact been observed.[18]

Although the U_3O_7 composition could be accommodated by the above cluster chain model no complete experimental determination of its crystal structure exists. Two modifications have been reported,[19–21] α-U_3O_7 and β-U_3O_7. The diffraction patterns of both forms have been indexed on the basis of tetragonal unit cells approximately isodimensional with that of UO_2, 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.

Although the next characterised oxide phase, α-U_3O_8, has an orthorhombic structure, it is possible that this and the UO_2 fluorite lattice tolerates non-stoicheiometry in a similar manner. Some evidence for this derives from a study of the reduction of α-U_3O_8 to α-U_3O_{8-z} by electron diffraction in which Sato *et al.*[22] proposed that the reduction of uranium(VI) to uranium(V) or uranium(IV) ions occurred in stages described in terms of a crystallographic out-of-step process during which slight positional alterations of the uranium atoms accompanied the change in oxidation state. The limiting stoicheiometry for both types of defect structure may occur at U_2O_5, the orthorhombic form obtained by Rundle *et al.*[23]

(*e*) *Implications of the New Crystal Structure.*—Previous models of the crystal structure of hyperstoicheiometric UO_{2+x} with $0 < x < \sim 0.2$ have been based on the uptake of oxygen by UO_2 as randomly distributed individual oxygen atoms or clusters. For $\sim 0.2 < x < 0.33$ the presence of a superlattice has been explained in terms of the long range ordering of oxygen clusters. In the model described in this paper, short range ordering in the form of cluster chains has been suggested for the first time. The implications for material transport processes, particularly diffusion, in hyperstoicheiometric oxides such as U_4O_9 and U_3O_7 could be far-reaching. The cluster chain represents a one-dimensional 'path' of different chemical and physical properties within the conventional fluorite matrix. For instance, the 10-fold co-ordination around a line of U^{6+} ions has been shown from bond length calculations to be more covalent than that existing between other uranium and oxygen atoms. Consequently atoms arranged in these chains present a greater barrier to diffusion than those occurring between chains. Qualitatively speaking therefore, the diffusion of foreign atoms through a highly hyperstoicheiometric phase of UO_2 may take place more readily in those regions between the cluster chains. In extreme cases an easy diffusion path may occur. For example, the release of fission gas from UO_2 fuel rods could be significantly affected by short range ordering of oxygen clusters in linear arrays.

The model proposed here could also assist theoretical treatments of electrical conductivity data. It has been suggested [11] that the classical band theory is inadequate to describe the conductivity mechanism. An alternative proposal involves the jumping of holes (or electrons) from one ion to a neighbouring ion. The holes are assumed to be localised at U^{5+} cations and not free to move through the lattice at low temperatures since they are bound to interstitial oxygen ions. At high temperatures, however, the holes become free and can move through the lattice. The mobility of the carriers increases since it is a thermally activated process involving hole jumps from U^{5+} to an adjacent U^{4+} cation. Thus the presence of U^{6+} rather than U^{5+} infers that a different conductivity mechanism is operating. Certainly the presence of cluster chains with linear arrays of U^{6+} ions implies that the mobility of the charge carriers will be different.

Conclusions

(*i*) A linear ordering of oxygen 2 : 2 : 2 clusters in chains parallel to the general directions ⟨110⟩ has been postulated to describe the ordered hyperstoicheiometric oxides of UO_{2+x} in the range $\sim 0.2 < x \leqslant 0.33$, (*ii*) an average chain spacing of ~13 Å is associated with the composition U_4O_9, and (*iii*) a new crystal structure for U_4O_9 has been suggested based on

cluster chains and the positions of all 832 atoms within a new unit cell have been determined.

Acknowledgements

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