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Point Defects in Uranium Oxides.

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Abstracts

In order to understand defect and impurity mechanism in UO_2 , we carried out the calculation of defect clusters of UO_2 in the one-electron approximation, using a semi-empirical tight-binding formalism. Two simple defect cluster models for the oxidation of UO_{2+x} , 2:1:2 and 2:2:2 cluster, were considered. The virtual crystal approximation (VCA) was applied to calculate the electronic structure for both clusters. We constructed the Green's function of the defect states and present quantities which are closely related to the Greens function. The local and total densities of states for uranium and two different types (dislocations and interstitials) of defect oxygen, O' , O'' are calculated. As excess oxygen entered the lattice three main changes were identified: (i) Fermi energies are shifted to higher energy ; 3.4 eV for 2:1:2 and 2.1 eV for 2:2:2. (ii) The peaks of total density of states are shifted to higher energy (iii) The small peaks of local density of states moved to midgap within the corresponding bulk band gap.

KEYWORDS : *point defects, defect clusters, tight-binding method, density of states, Fermi energy, uranium dioxide.*

I. Introduction

Interest in UO_2 is stimulated both by the diversity of the fundamental properties

associated with the materials and by the important technical problems associated with its use as a reactor fuel. However, in spite of various experimental results as well as theoretical ones [1-6] , relatively little is still known about its electronic structure.

The validity of any model for the electronic structure is determined by its agreement with experimental results. The tight-binding model has a distinct advantage in this respect over other techniques, since one can obtain a better representation of the electronic structure by semiempirical fit to the experimental measurements. Also, the parameters of the model have a strong chemical meaning, representing effective atomic energies and bond strengths. The results are interpretable as physical quantities such as valences and local densities of states.

We investigate the electronic structure of the non-stoichiometric defect clusters in uranium dioxide based upon the result of bulk state calculations. The details of the defect models are sensitively dependent on the geometry of the atoms or ions involved. Thus we investigate defect states of two typical defect clusters, 2:2:2[7-8] and 2:1:2[9] cluster. We concerned here principally with the charge states of anion defects and of the electronic defects present in the non-stoichiometric phase.

II. Calculations

1. Defect Models.

Two simple defect cluster models for the oxidation of UO_{2+x} are considered here. On oxidation of UO_2 to UO_{2+x} defect clusters are formed in the oxygen sublattice. As oxygen is added to $\text{UO}_{2.00}$ in the unit cell to produce UO_{2+x} , the fluorite cell contracts, in which excess oxygen is initially incorporated interstitially in 2:1:2 clusters and with an increase in $x(x=0.12)$ for UO_{2+x} , the formation of 2:2:2 cluster is formed. At the limiting composition ($x=0.25$), the disordered UO_{2+x} phase changes to an ordered phase, $\text{UO}_{2.25}$ or U_4O_9 . For both clusters the presence of the interstitial oxygen, O' , displaces the lattice oxygen, O'' and normal oxygen, O . Thus, three types of defects occur: interstitial oxygen at O' and O'' sites and normal oxygen vacancies, O .

Although the cation lattice remains fixed in position, some cations are now surrounded differently from the bulk lattice uraniums. For example there are three different cation sites; U_1 , where the cation is in a lattice site essentially unassociated with an interstitial cluster; U_2 , the two uranium ions immediately adjacent to the O' ; U_3 , the four cations closely associated with the displaced O'' .

Thus the oxygen environments for U_2 and U_3 are different for the two clusters, 2:1:2 and 2:2:2. This gives the difference of possible intervalence transitions within the two clusters.

3. Density of States.

The Green's function, which expresses all of the necessary information about perfect crystal, is obtained from LCAO calculation. It is given in the spectral representation[10] by

$$G^{(0)}(E) = \sum_{k,n} W_k \frac{\Psi^+(\vec{k}, n) \Psi(\vec{k}, n)}{E - E(\vec{k}, n) + i\delta} \quad (1)$$

, where $E(\vec{k}, n)$ and $\Psi(\vec{k}, n)$ are the electronic eigenvalue and the wave function in the tight-binding representation for the n^{th} band and one of the N sample wave vectors \vec{k} with weight W_k within the irreducible part of the Brillouin zone[11].

For these calculations, the sum is taken over $N=27$ sample points for the fcc structure. A finite value of $\delta=0.2$ eV was used, smoothing the results with a Lorentzian line shape. The total density of states is simply the sum of the local densities of states of each atom in the unit cell.

The local density of states for both spins is calculated from the Green's function $G^{(0)}$ associated with unperturbed bulk crystal,

$$\rho^{(0)}(E) = -\frac{1}{\pi} \text{TrIm} | G^{(0)}(E) | \quad (2)$$

,where Tr indicates a trace over those orbitals associated with a given site and Im means the imaginary part of $|G^{(0)}(E)|$.

The Fermi energy is calculated by integrating the total density of states up to the number of valence electrons for each material which is consistent with a average of the highest occupied energy states across the sample wave vectors.

The local and total density of states in the defect clusters are calculated by perturbed Greens function G , which is determined through the Dyson's equation, viz.,

$$G = G^{(0)} + G^{(0)}VG \quad (3)$$

Then the density of states of introducing the defect potential V due to interstitials and vacancies is calculated by the relation.

$$\rho(E) = -\frac{1}{\pi} \text{TrIm} | G(E) | \quad (4)$$

The tight-binding parameters for defect calculation are determined from the above bulk state calculation. The tight-binding parameters for defect calculation are determined from the above bulk state calculation.

The average cell belongs to the space group $Fm\bar{3}m$, and the interstitial of the oxygen O' , is displaced along any of the twelve $\langle 110 \rangle$ direction from $(1/2, 1/2, 1/2)$ and the interstitials oxygen O'' is placed from the same position along any of the eight $\langle 111 \rangle$ directions[12]. The 2:2:2 defect complex contains two O' interstitial atoms and O'' interstitial atoms and two vacancies in the lattice oxygen sublattice as shown in Fig.2. The calculation for the defect complex is performed not in the periodic supercell $(2 \times 2 \times 3)$, but 2:2:2 cluster within supercell by allowing the interaction with all nearest neighboring atoms. Our calculation indicates that the defect atoms (O', O'') introduce extra electronic levels within the energy gap as shown in Fig.5. Such defects not only give carriers that are easily freed and so increase the conductivity, but also change the Fermi level in the solid. Those defect levels are derived from U_{7p} , U_{6d} of O'' orbitals as shown Fig.5. The pinning level for U_{7p} in the gap is about 3 eV below the conduction band and for O''_{2p} in the gap is about 0.3 eV above the valence band. Thus, the nature of inter-band thermal excitation can be explained by these defect energy levels.

II. Results and discussion

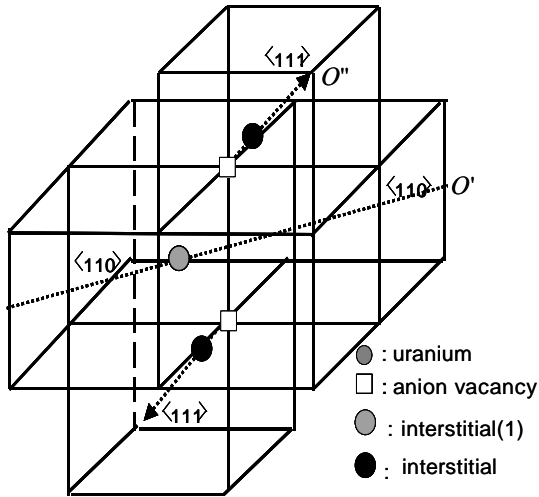


Fig.1. 2:1:2 cluster

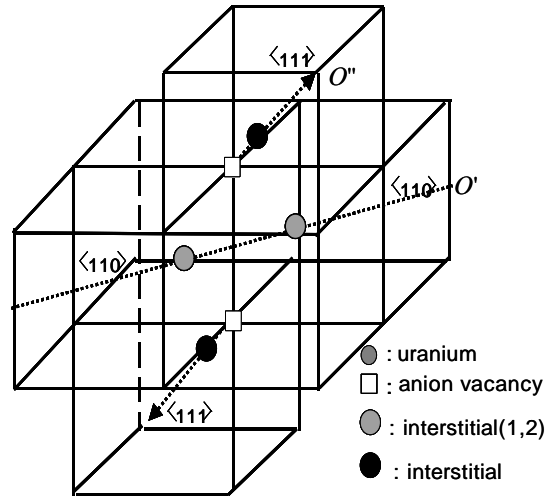


Fig.2. 2:2:2 cluster

From the result of our calculations(Fig.3. ~Fig.5.) the defect cluster calculation shows that defect levels for interstitial atoms are pinned within the band gap and this result indicates that the conductivity of uranium oxide will be drastically modified by the injection of vacancies and interstitials in UO_2 . In hyperstoichiometric UO_{2+x} , the conduction occur by a mechanism of hole hopping[13]. Aronson et al[14]. have shown that the electrical conductivity for UO_{2+x} can be represented by an equation involving an activation energy of E_a of 0.3 eV. Values of the activation energy from several experiments range from 0.17 to 0.34. From the Fig.4. we can see that the defect levels in 2:2:2 cluster are derived from U_{7p} is about 0.3 eV above the valence band, which indicates hole hopping conductivity mechanism. However, we can see from Fig.3. that the defect levels in 2:1:2 cluster are derived from U_{6d} is 0.5 eV above the valence band

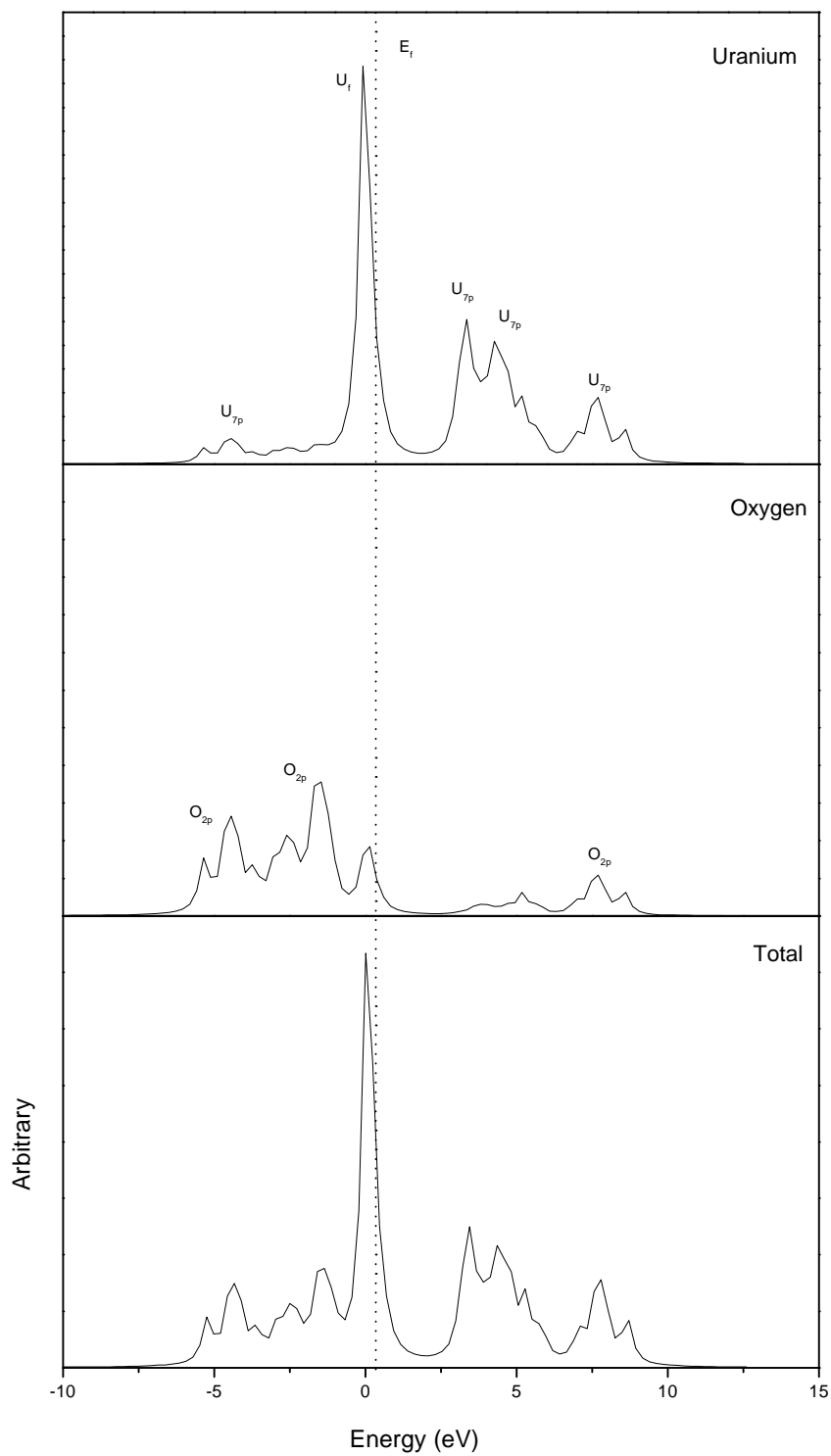


Fig.3. Local and total density of states in bulk state

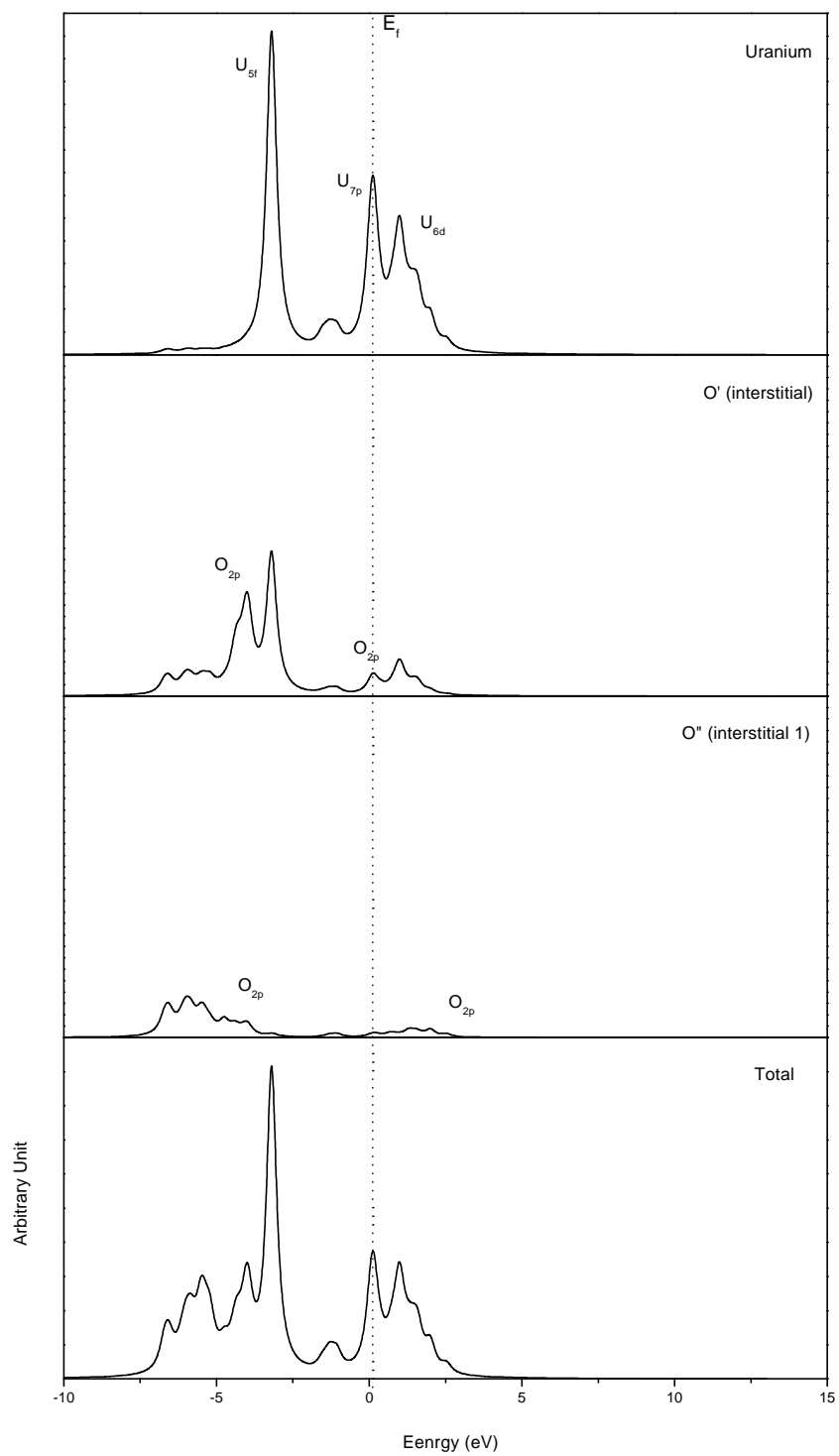


Fig.4. Local and total density of states in 2:1:2 cluster

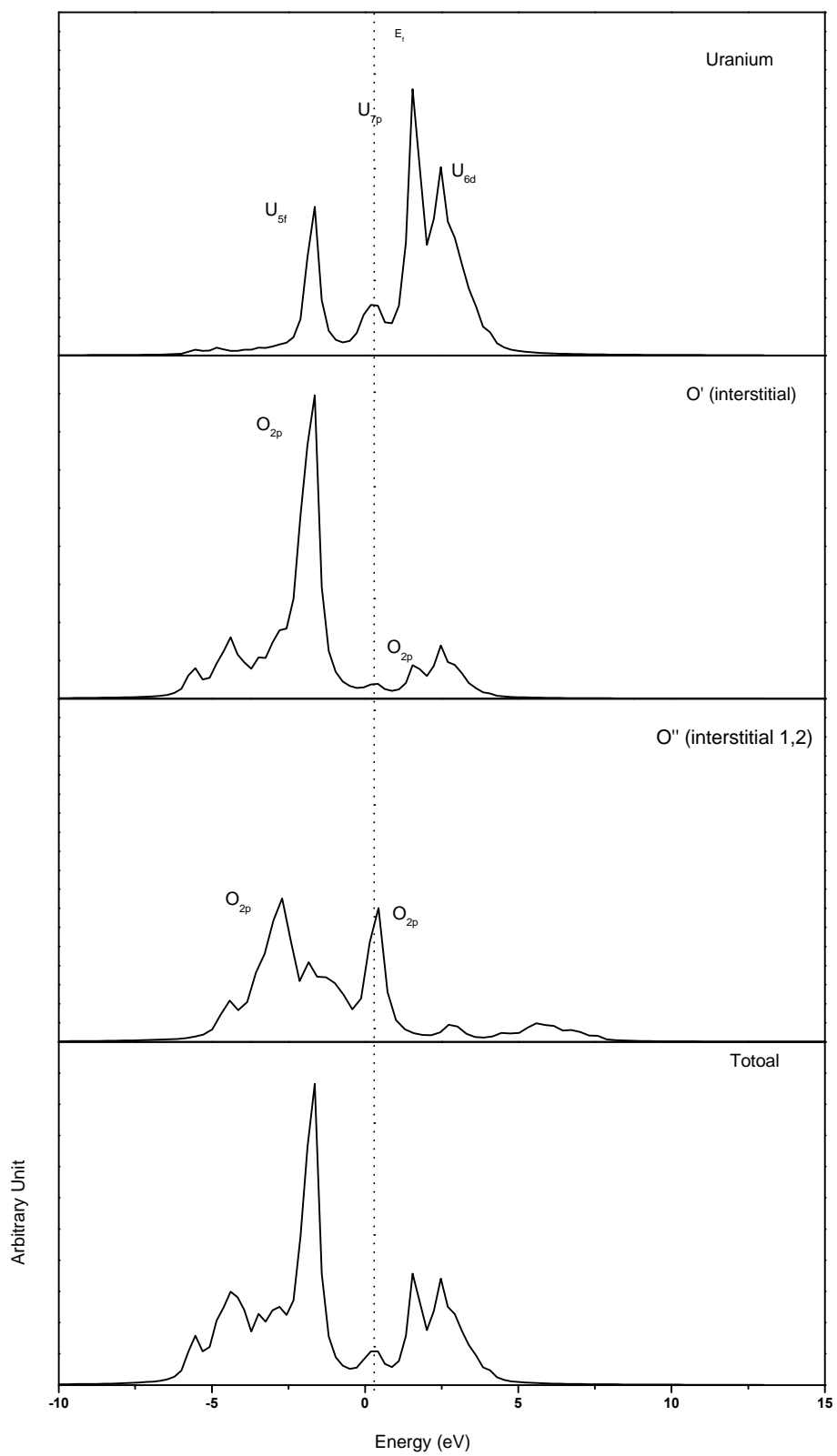


Fig.5. Local and total density of states in 2:2:2 cluster

2:1:2 cluster						2:2:2 cluster					
orbitals	U _{5f}	U _{7p}	U _{6d}	O' _{2p}	O'' _{2p}	orbitals	U _{5f}	U _{7p}	U _{6d}	O' _{2p}	O'' _{2p}
energy (eV)	-3.2	0.2	1.0	-3.2	-6.0	energy (eV)	-1.7	1.5	2.5	-1.7	-4.2

Table.1 Locations of peak in the local density of states for both clusters.

Acknowledgement

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