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Alain Pasturel, Florence Gupta, Guillaume Brillant

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Correlation effects and Energetics of
point defects in uranium dioxide: a first principle investigation

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Abstract:

Density functional (DFT) calculations have been used to investigate the stability of point defects in uranium dioxide. Correlation effects are taken into account within the DFT+U approach as implemented in the Vienna Ab initio Simulation Package (VASP). More particularly the formation energies of both intrinsic and extrinsic point defects, i.e. vacancies, interstitials, Frenkel pairs and Schottky trio defects are calculated. Our results are compared with available experimental data and are also discussed in relation to previous calculations based on conventional functionals such as the local spin-density approximation and generalized gradient approximations.

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I.   INTRODUCTION:

Uranium dioxide (UO_2) is of long-standing interest to material scientists due to the diversity of the fundamental problems associated with the material and by the important technological problems arising from its use as a reactor fuel cell. UO_2 is known to be an antiferromagnetic insulator [1, 2] with an optical gap of roughly 2 eV. However it is also known that its transport properties, both atomic and electronic, as well as thermodynamic properties, are greatly influenced by the deviations from stoichiometric composition, which are caused by the occurrence of point defects. More particularly, such defects can modify the crystal structure, cause a swelling of the solid and also may constitute traps for fission gases or helium. Then they have a direct impact on thermomechanical, structural an kinetic properties of the material, especially under irradiation.

In view of the importance of UO_2 and of the difficulty that is found in experimental studies (particularly under the extreme conditions of the nuclear industry) there is a need for reliable theoretical calculations of defect formation and migration energies. The first theoretical studies of point defect formation energies were based on interionic empirical potentials using the Mott-Littleton methodology [3-5]. However the calculated formation energies of uranium Frankel pair and that of Schottky trios present an important discrepancy (about a factor of 2) with experimental values deduced from diffusion coefficient measurements [6]. Such an overestimation is essentially due to the use of formal ions charges to describe cohesive properties of partially covalent oxides. More recently, ab initio calculations, based on the density functional theory (DFT) were used to calculate formation energies of point defects in UO_2. In these calculations, the major problem is that both the local density approximation (LDA) and the generalized gradient approximations (GGA) give a qualitatively incorrect description of the strongly correlated 5f states of U, leading to metallic instead of insulating behaviour of UO_2 [7-9]. To correct these well known failures of the conventional DFT based calculations, more sophisticated functionals were introduced recently to describe the insulating behaviour of UO_2. For instance, calculations using hybrid DFT functional [10, 11] give results in very good agreement with experimental photoemission data. The self-interaction correction is also known to correct this kind of problems [12]. Dudarev et al. [13] showed that DFT+U method yields the correct insulating ground state. Very recently,

Laskowski et al. [14] used this approach to investigate the magnetic structure and electric-field gradients of UO_2.

Since the DFT+U method is able to provide a correct description of magnetic and thermodynamic properties of UO_2, our purpose is to extend such calculations to formation energies of point defects. In section 2, we present the details of the DFT+U method. In section 3, we present formation energies of point defects in UO_2. They are discussed in comparison with the available experimental data and other theoretical results based on LDA or GGA functionals. Finally section 4 summarizes our conclusions and presents our perspectives.

II.   METHOD :

Total energy calculations were performed with the projector-augmented-wave method [15] as implemented in the Vienna Ab initio Simulation package [16]. The effects due to the localization of the f electrons of uranium in UO_2 are taken into account with the GGA+U approximation as recently implemented in VASP [17, 18]. In the so-called GGA+U approximation, the spin-polarized GGA potential [19] is supplied by a Hubbard-like term to account for the quasiatomic character of the localized (here 5f) orbitals. Hence the localized electrons (5f) experience a spin- and orbital-dependent potential, while the other orbitals are delocalised and considered to be properly described by GGA. The rotationally invariant form of GGA+U is used with a spherically averaged double counting term [20]. Within this approximation, there is a single parameter U_{eff} which is chosen to be equal to 4 eV for all the studied compounds. Such a value is also very close to the value used by Dudarev et al. [13] or by Laskowski et al. [14] and to the experimental findings [21, 22].

A plane-wave basis set with a cutoff energy of 400 eV was used in all calculations. Brillouin zone sampling was performed using a 16x16x16 k-point grid for the 12-atom primitive cell. This primitive cell allows studying the antiferrromagnetic ground state of UO_2. The layered antiferromagnetic (AF) structure (see Fig.1) was assumed to be the one observed experimentally [2]. Such a k-point grid is found appropriate for total energies and magnetic moments to converge within 10^{-3} eV and 0.01 μ_B respectively. Point defects were modelled using periodically repeated supercells consisting of 2x2x2 primitive cells (96 atoms) with the number of k points reduced accordingly. Structural optimizations were performed at constant volume and under the condition that all residual forces should be smaller than 0.01 eV/Å. The equilibrium properties of UO_2 [cohesive energy, volume and density of states (DOS)] correspond to the ground-state configuration for the atomic and electronic degrees of freedom.

III.   RESULTS AND DISCUSSION::

3.1 Pure compound UO_2:

We first investigate the structural and thermodynamic properties of UO_2 (fluorite structure, space group Fm3m). The equilibrium structure was determined by calculating the total energy for several different lattice parameters and fitting data to Birch-Murnaghan's equation of states. Three series of calculations were performed using different functionals, i.e. GGA, spin-polarized GGA (AF-GGA) and GGA+U. All the results are gathered in Table I. In contrast to previous results in the LDA [13], the GGA analysis shows that the antiferromagnetic structure is predicted to be the most stable structure. The calculated value of the magnetic moment localised on a uranium ion at equilibrium was found to be 1.44 μB, which is about 17 % smaller than the value observed experimentally [2]. Compared to experiments, both GGA and AF-GGA give equilibrium lattice constants smaller than the experimental one while calculated cohesive energies are slightly larger than the experimental value. This latter overestimation is a well-known feature of GGA treatment. Consistent with prior research [9, 23], both GGA and AF-GGA give a metallic electronic structure, where the U 5f bands are partially occupied (see Fig 2 a). In contrast, calculations using the GGA+U approach predict the correct insulating ground state with an energy band gap of 1.8 eV in close agreement with the value observed experimentally (see Fig. 2b). Our analysis suggest that the insulating nature of the ground state results from taking better account of the effect of electron-electron correlations in the 5f band, in agreement with other theoretical analysis [13, 23]. Within the GGA+U approach, the magnetic moment of each U ion becomes 1.94 μB. Table I shows that the predicted lattice value constant is slightly larger than the experimental one while the calculated cohesive energy is smaller than the experimental one by about 6 %. All these results are consistent with weaker covalent bonding and suggest that the inclusion of correlation between 5f electrons indeed leads to this decrease binding. These findings may have also important implications for formation energies of point defects in UO_2, characterized by the presence of strong correlations between valence electrons.

3.2 Point Defects:

- **Isolated Point Defects:**

In the following, we consider neutral point defects, i.e. isolated vacancies and interstitials of uranium and oxygen. As already mentioned above, these point defects were modelled using periodically repeated supercells consisting of 2x2x2 primitive cells (96 atoms). This corresponds to a defect concentration of $c_U = 1/32$ and $c_O = 1/64$. A specific supercell was built for each type of point defect. More particularly, the uranium interstitial has been chosen to be octahedrally coordinated. According to Willis [27], three different interstitial sites for oxygen have been considered: (i) the center of an oxygen cube O(0), (ii) the O(1) position is half way from the center of an oxygen cube and from the line joining two adjacent oxygen atoms. (iii) the O(2) position lies in the middle of the line joining the center of an oxygen cube and a summit of this cube.

The free energy of formation of an isolated point defect is defined as the free energy between the system with and without the defect:

$$\Delta G_f = \Delta E_f - T\Delta S_f + P\Delta V_f \qquad (1)$$

Here ΔE_f is the change in total energy (including chemical potentials), ΔS_f is mainly the change in vibrational entropy, and ΔV_f is the change in volume effects when the defect is introduced into the system. As the defect concentration is small, the contribution of volume changes is small. When a defect is introduced, the associated change in the vibrational contribution has two distinct contributions: the defective lattice has a different number of vibrational modes compared with the perfect crystal; (ii) the frequencies of the remaining modes may change in the presence of the defect. However this contribution is known to be small and will be neglected. Then we focus only on computing formation energy terms. When investigating defects that change the composition of a material, the formation energies are usually evaluated with respect to a set of fixed external chemical potentials for the atomic species involved. The results will then depend on the actual values of these atomic chemical potentials. To be consistent with previous theoretical calculations, we chose for reference states the elements in their standard states, i.e. oxygen molecule and α-uranium. Then free energies of formation for oxygen defects (oxygen interstitial: I_O and oxygen vacancy: V_O) can be written as:

$$\Delta E^f_{\left(\frac{V_O}{I_O}\right)} = E^{96\mp1}_{\left(\frac{V_O}{I_O}\right)} - E^{96} \pm \mu_O \tag{2}$$

$$\text{and}\quad \mu_0 = \tfrac{1}{2}\mu_{O_2} = \tfrac{1}{2}\left[E_{O_2} + kt\ln(f(T) + kt\ln\left(\frac{P_{0_2}}{P^0}\right) \right] \tag{3}$$

where the pressure reference state $P^0 = 1$atm, and E_{O_2} is the total energy of an isolated oxygen molecule that can be obtained from DFT calculations. Let us mention that the two last terms of equation (3) give a non negligible dependence of the free energy of formation of oxygen defects as a function of temperature and pressure. This dominating contribution to the free energy of formation then comes from the entropy increase associated with the release of gas molecules to the atmosphere.

The free energy of formation of uranium defects (uranium interstitial: I_U and uranium vacancy: V_U) are:

$$\Delta E^f_{\left(\frac{V_U}{I_U}\right)} = E^{96\mp1}_{\left(\frac{V_U}{I_U}\right)} - E^{96} \pm \mu_U \tag{4}$$

Let us mention that the U and O chemical potentials are not independent but must satisfy the equilibrium condition with UO_2 bulk compound:

$$\mu_U + \mu_O = F_{UO_2} \approx E_{UO_2} \tag{5}$$

then the free energies of formation of the uranium defects depend also on both temperature and the oxygen pressure.

Table II gives the internal energies of formation of oxygen and uranium defects in UO_2. They are also compared to previous ab initio based results.

We can see a qualitative agreement between the different sets of values. More particularly, for all the calculations, the formation energy of oxygen interstitials is predicted to be negative. This result means that UO_2 compound is instable in presence of oxygen vapour, the incorporation of oxygen atoms occurring at the interstitial site of the fluorite structure. It is in agreement with the fact that UO_2 spontaneously becomes oxidized in air at temperature as low as 120°C []. All other defects present positive formation energies. A quantitative comparison with the results of Petit et al. [] is difficult since their calculations are based on a very crude

description of the charge density of the material. On the other hand, our GGA calculations are in correct agreement with those of Freyss et al. [].

Formation energies of the uranium interstitials and vacancies seem to be quite sensitive to the approximations made to describe the electronic ground state of UO_2. Including spin polarization effects to describe the antiferromagnetic order modify the formation energies of the uranium defects mainly; it is not so surprising since the antiferromagnetism is governed by the spin-polarization of the partially filled U 5f bands. Including the Hubbard treatment reinforces this effect since the magnetic moment of each uranium ion becomes still more important.

Willis [27-28] finds by neutron diffraction measurements that oxygen interstitials in UO_{2+x} occupy two other types of interstitial sites. One type, O(1) is displaced by about 1 Å from the center of oxygen cube, i.e. the octahedral site O(0), and along a <110> direction whereas the other type, O(2) is displaced by about the same amount along the <111> direction. In fact the formation of these interstitials is directly related to the formation of "defect clusters". The simplest one used by Willis to explain neutron diffraction data is the 2:2:2 cluster that contains two O(1) interstitials, two O(2) interstitials and two normal oxygen vacancies. If the structural stability of such "defect clusters" is beyond the scope of this study, we present preliminary results concerning the stability of the oxygen interstitial in the three mentioned interstitial sites. After relaxation, we find that both O(1) and O(2) sites are energetically more favourable than the O(0) site, using the GGA+U approach. The gain in energy is quite similar, namely 0.6 eV/atom and the displacement is about 0.03 Å from the exact center of the cube. Let us mention that relaxation effects lead also to a deformation of the oxygen cage. Such relaxation effects, not observed using conventional functionals and which can be attributed to a better treatment of electron-electron correlations, will be investigated in future work.

- **Defect interactions:**

We will finally present data and discuss the consequences of interactions between point defects in UO2. The most common approach to calculate the formation energies for more complex defects like Frenkel pairs, which consist of a vacancy and an interstitial of the same chemical type, and Schottky defects, which consist of two oxygen vacancies and one uranium vacancy, is to assume that vacancies and interstitials forming these defects are non-interacting. In this case, the formation energy of a Frenkel pair (FP) of U (or O) specie is given by:

$$\Delta E^{f}_{FP(U,O)} = E^{95}_{V(U,O)} + E^{97}_{I(U,O)} - 2E^{96} \tag{6}$$

and for the Schottky defect (S) by:

$$\Delta E^{f}_{S} = E^{95}_{V(U)} + 2E^{95}_{V(O)} - 3\frac{95}{96}E^{96} \tag{7}$$

The formation energies of these defects with the assumption of isolated point defects are reported in Table II. They are compared to previous theoretical results and also to values obtained by Matzke [6] from diffusion measurements. Let us mention that the experimental analysis of the populations of defects in UO_{2+x} were performed using the point defect model (PDM), based on the assumption that the defects giving non-stoichiometry are isolated point defects. We can see that all theoretical results agree on predicting the larger stability of oxygen Frenkel pairs over uranium Frenkel pairs and Schottky defects. One can note also that the predicted formation energies of Frenkel pairs and Schottky defects are in the range of experimental data although calculations seem to overestimate the formation energy of the uranium Frenkel pair. However, let us mention that the experimental value of the uranium Frenkel pair given by Matzke [6] has been determined indirectly. Indeed it has been estimated from the measured formation energy of the oxygen Frenkel pair and the measured self diffusion activation energies of both oxygen and uranium by assuming that the oxygen point defects are dominant and point defects are isolated and non interacting.

To check the influence of interactions between point defects, we have calculated the formation energies of the uranium and oxygen Frenkel pairs using the LDA+U approach and the 96 atom supercell in which the vacancy and the interstitial forming the pair are either as far separated as possible (taking periodicity into account) or nearest neighbour. In the first case, the formation energies are equal to 10.2 and 2.8 eV for uranium and oxygen Frenkel pairs respectively. These values are slightly less positive than those obtained from Equ. (6), indicating that the vacancy and the interstitial forming the Frenkel pair display weak attractive interactions. In the second case, when the two point defects are nearest neighbour, the findings are 0 eV for both Frenkel pairs. These results show that the interstitial atom (U or O atom) moves to the vacancy position without any barrier energy, emphasizing that such

Frenkel pairs with this peculiar geometry do no exit in UO_2, contrary to Petit et al.'s assumptions [7]. Let us mention that the same behaviour is also observed for the Schottky defect with an interaction energy ranging from -4.2 to -5.1 according to the geometry of the Schottky trio (the negative sign means that the defects tend to attract each other). All these preliminary results show that the point defects may be in strong interactions according to their respective locations. We think that such attractive interactions play a key role in the stability of the so-called Willis clusters.

IV. SUMMARY AND CONCLUSIONS:

In conclusion, we find that DFT+U improves on the traditional density functionals, providing a first-principles description of UO_2 in good agreement with experiment. This success is explained by the better treatment of the f-electron localization, which is responsible for the non zero band gap. Our calculations of formation energies of point defects show that this f-electron localization modify formation energies of uranium point defects more strongly than those of oxygen ones. Another important result is that the formation energies of Frenkel pairs and Schottky defects are very sensitive to defect interactions and then to the geometry of these defects. Therefore the assumption of non interacting defects commonly used in the literature must be considered very carefully. Further studies of more complex systems, such as "defect clusters" observed by experiments and suggested by our preliminary calculations as being energetically favourable, should be of interest. We believe that the results presented in this paper illustrate the usefulness of first-principles based calculations in elucidating complex structural behaviour in non-stoichiometric compounds.

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Figure Captions:

Figure 1: Fluorite crystal structure of UO_2. Oxygen sites are in grey, uranium sites are shown in black. The antiferromagnetic ground state is characterized by the network of arrows.
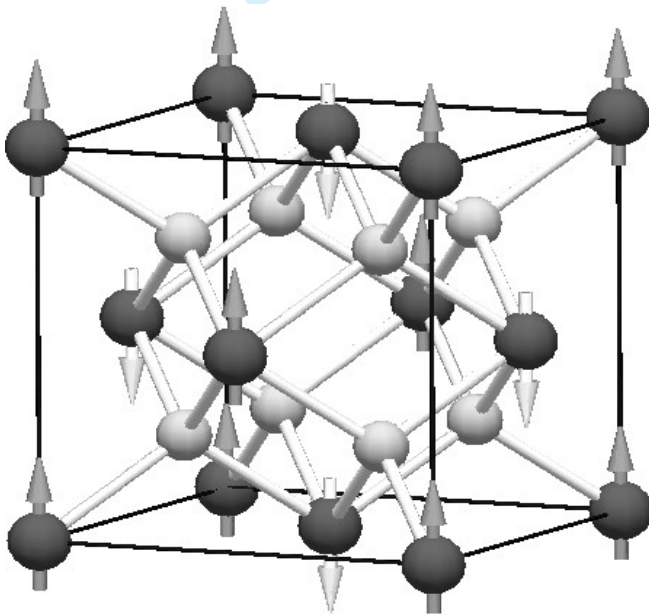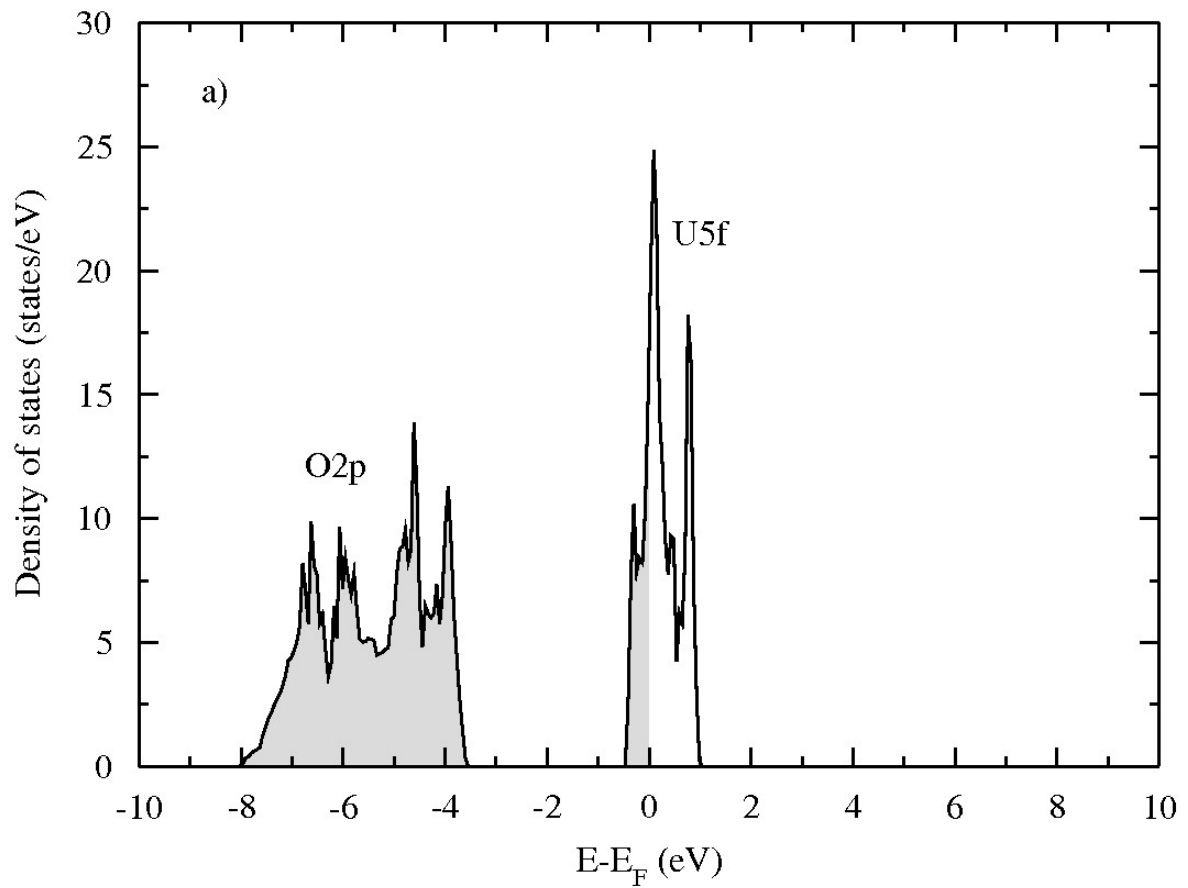
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Figure 2: Total electronic DOS of UO_2:   a) AF- GGA results.   b) GGA+U.
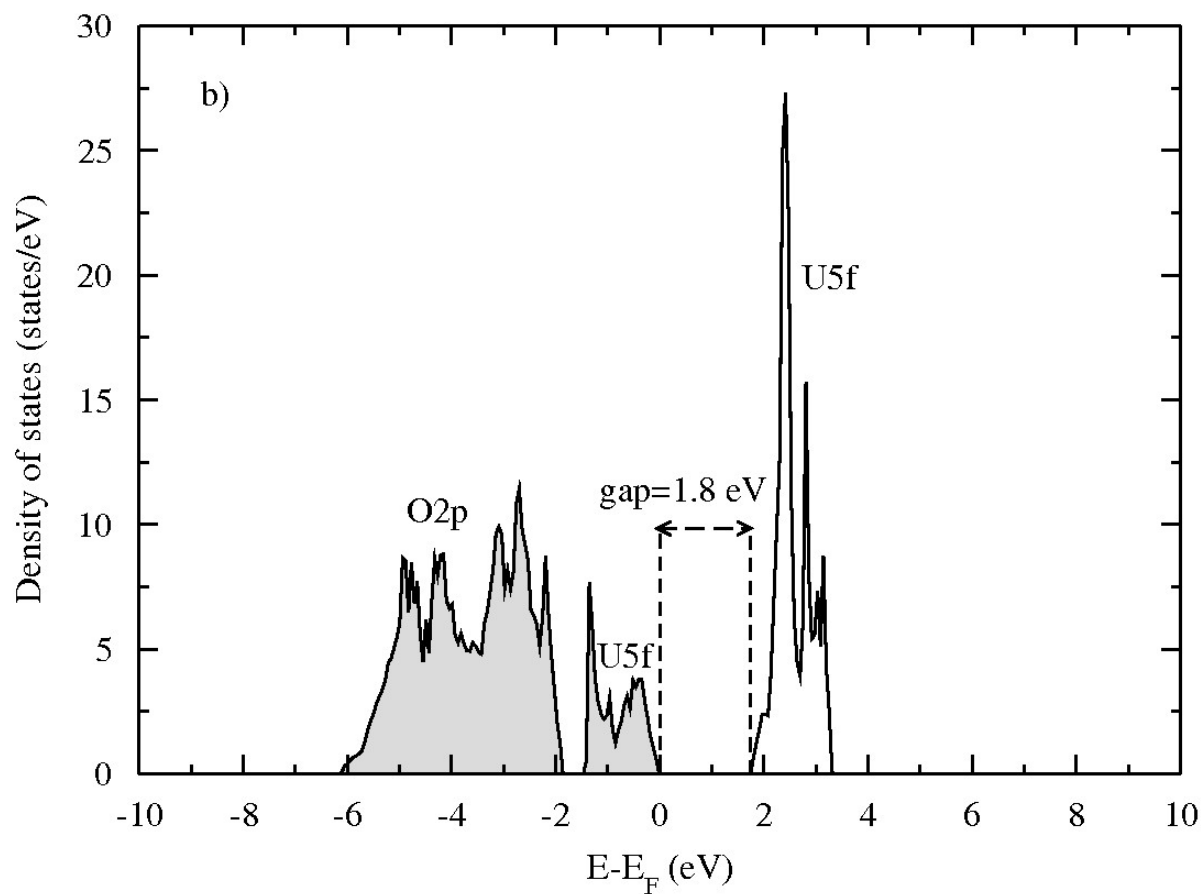
Table I: The experimental and calculated properties of UO_2 obtained from different functionals i.e. GGA, AF-GGA and GGA+U.

	GGA	AF-GGA	GGA+U	Experiment
Lattice constant (A)	5.38	5.40	5.52	5.47 [24]
Cohesive energy (eV/UO_2)	23.58	23.62	21.71	22.31 [25]
Bulk modulus (GPa)	209	188	209	207 [26]
Magnetic Moment (μB)	0	1.44	1.94	1.74 [2]
Band gap (eV)	0	0	1.8	1.8 [1]

Table II: Formation energies (eV) of point defects in UO2; uranium and oxygen vacancies (U-Vac and O-Vac), uranium and oxygen interstitials (U-Int and O-Int). Frenkel pairs (O-Fp and U-FP), and Schottky defect (S) are calculated as being non-interacting defects.

Formation energy (eV)	U-Vac	O-Vac	U-Int	O-Int	O-FP (model)	U-FP (model)	S (model)
GGA	4.0	6.1	6.0	-2.5	3.6	10.0	5.2
AF-GGA	4.4	6.1	6.5	-2.6	3.5	10.9	5.5
GGA+U	6.0	5.6	8.2	-1.6	4.0	14.2	7.2
LDA [7]	19.1	10.0	11.5	-3.3	6.7	30.6	17.1
LDA [8]	3.3	6.7	7.3	-2.9	3.8	10.6	5.8
GGA [9]	4.8	6.1	7.0	-2.5	3.6	11.8	5.6
Experimental [6]					3.0-4.6	9.5	6.0-7.0