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Plane-wave pseudopotential study of point defects in uranium dioxide

J. P. Crocombette,[1,*] F. Jollet,[2] L. Thien Nga,[2] and T. Petit[3]
[1]*Service de Recherches de Métallurgie Physique, CEA Saclay, 91191 Gif/Yvette cedex, France*
[2]*CEA, Centre d'Etudes de Bruyères le Châtel, BP 12, 91680 Bruyères le Châtel, France*
[3]*CEA, Direction des Réacteurs Nucléaires, Département d'Etudes des Combustibles, Service d'Etudes et de Simulation du Comportement du Combustibles, Centre d'Etudes de Cadarache, 13108 St. Paul Lez Durance Cedex, France*

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A study on uranium and oxygen point defects in uranium dioxide using the *ab initio* plane-wave pseudopotential method in the local density approximation of the density functional theoretical framework is presented. Norm conserving pseudopotentials are used to describe oxygen and uranium atoms. The uranium pseudopotential is specifically described. Its validity is ascertained thanks to a detailed structural study of uranium dioxide and of three phases of metallic uranium (fcc, bcc, and α phase). The free energies of formation of both intrinsic (Frenkel pairs and Schottky defect) and extrinsic (single vacancies or interstitials) defects are calculated. The obtained values form a reliable set of numerical data that are analyzed in the framework of the point defect model which is commonly used to assess defect concentrations in uranium dioxide and their variation with stoichiometry. From the obtained results, the ability of the point defect model to accurately reproduce defect concentrations in uranium dioxide is discussed.

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I. INTRODUCTION

Uranium dioxide is a key material for nuclear industry. It is indeed the usual fuel for pressurized water reactors. In operation in power plants or in the context of direct disposal of spent fuel, a clear understanding of its thermomechanical, structural, and kinetical properties is very important. Point defects are of major importance for these properties especially under irradiation. From the theoretical point of view, point defect formation energies have been calculated mainly using empirical potentials.[1–3] To our knowledge only one *ab initio* electronic structure study has been published on that subject.[4] In that study, the linear muffin tin orbital method in the atomic sphere approximation LMTO-ASA was used in the framework of density functional theory in the local density approximation DFT-LDA. In the present work we study point defects in uranium dioxide in the same framework using the plane-wave pseudopotential approach. This approach is very well suited for point defect studies as it can deal with inhomogeneities of atomic density such as the one introduced by point defects and allows to include structural relaxation around defects.[5] Up to now it has not been applied to actinides compounds, for which obtaining a good pseudopotential was a difficult prerequisite. We thus had to generate a pseudopotential to describe the uranium element.

In the first part of the paper the characteristics of this pseudopotential are described and its ability to reproduce the different phases of metallic uranium and that of UO_2 is presented. A special attention has been paid to the α phase of uranium which is the stable one at ambient conditions. U-α phase is base centered orthorhombic with two atoms per unit cell. One thus has the delicate task to optimize three structural parameters besides the equilibrium volume: b/a, c/a, and the internal parameter y. Based on the experimental observation[6] that the y and b/a parameters do not vary with pressure, the formerly published calculations optimize a and c/a only.

In the second part we tackle the study of isolated point defects in UO_2. Interstitials and vacancies of uranium and oxygen are considered. The atomic configurations around the point defects are calculated using the supercell method. From the calculated energies of the supercells we deduce the formation energies of intrinsic point defects: Frenkel pairs and Schottky defect. The free energies of formation of the extrinsic point defects (single vacancy or interstitial) are expressed as a function of the oxygen chemical potential (or outer dioxygen pressure). The obtained values are then analyzed using the point defect model which is of common use to assess the concentrations of defects in uranium dioxide and their variations with stoichiometry. From both the obtained results and recent experimental data, the ability of the point defect model to accurately reproduce defect concentrations in uranium dioxide is discussed.

II. GENERATION AND VALIDATION OF THE URANIUM PSEUDOPOTENTIAL

A. Generation of the pseudopotential

Uranium pseudopotential has been generated in the DFT-LDA framework using Perdew and Zunger[7] functional for the exchange-correlation term. The same functional has been used in all subsequent calculations. We employed the Troullier-Martins[8] method to generate the norm conserving pseudopotential. The electronic configuration of atomic uranium is $6s^2 6p^6 6d^1 5f^3 7s^2$. The pseudopotential has been obtained from an ionized electronic configuration: $6s^2 6p^6 6d^1 5f^3 7s^0$ with cutoff radii equal to 1.26 atomic units (a.u.), 1.52 a.u., 2.20 a.u., and 1.26 a.u. for s, p, d, and f angular momentum. The pseudopotential electronic levels deviate from the scalar relativistic all electron ones by less than 0.05 eV except for the $7s$ level where the deviation is 0.3 eV. The p component of the pseudopotential has been chosen as the local potential and a Kleinman-Bylander[9] form has been used.

TABLE I. Convergence of the uranium total energy per atom as a function of the cutoff energy E_c for the fcc (28 k points), bcc (70 k points), and α (64 k points) phases.

E_c(Ry)	120	140	160	180
E_α(Ry)	-103.00476	-103.01960	-103.02482	-103.02600
E_{bcc}(Ry)	-102.99384	-103.00821	-103.01332	-103.01451
E_{fcc}(Ry)	-102.98921	-103.00377	-103.00889	-103.01011
$E_{\mathrm{fcc}}-E_\alpha$(Ry)	0.01555	0.01583	0.01593	0.01589
$E_{\mathrm{bcc}}-E_\alpha$(Ry)	0.01092	0.01139	0.01150	0.01149

All the calculations dealing with metallic uranium have been made with the ABINIT[10] code, that is based on pseudopotentials and plane waves. It relies on an efficient fast Fourier transform algorithm[11] for the conversion of wave functions between real and reciprocal spaces, on the adaptation to a fixed potential of the band by band conjugate gradients method[12] and on a potential-based conjugate gradient algorithm for the determination of the self-consistent potential.[13]

B. Validation of the pseudopotential on uranium phases: bcc, fcc, and α

In the calculations on metallic uranium, a Gaussian smearing of 0.02 ryd has been applied for the integrations in the Brillouin zone. The convergence of total energy with the number of k points in the irreducible Brillouin zone (IBZ) has been tested for each phase. The obtained accuracy is better than 4.10^{-4} ryd for 28 k points in the fcc phase, 70 k points in the bcc phase and 64 k points in the α phase. In Table I the convergence with cutoff energy (E_c) for each phase and the energy difference with the α phase are indicated. The total energy converges at 1.2 mryd for $E_c=180$ ryd. However, it can be seen that differences in energy between the phases are converged within 0.4 mryd at $E_c=120$ ryd. Moreover, we checked that the equilibrium volume (V_0) and the bulk modulus (B_0) of the fcc phase were converged at 120 ryd. Therefore, the comparison between the three phases has been made at $E_c=120$ ryd. Calculated equilibrium volumes and bulk moduli are given in Table II. We have verified that a FP-LMTO (full potential linear muffin tin orbitals) calculation gives the same results for the fcc phase. Moreover, these results are in very good agreement with the one of a LDA full potential linear augmented plane-wave (FLAPW) calculation.[14] This agreement validates our pseudopotential. Furthermore the α phase is found to be the stable one in agreement with experimental facts (see Fig. 1).

C. Structural study of the U-α phase

To our knowledge, no complete study of the fully relaxed structure of uranium α phase has been carried out up to now. This is due to the relative complexity of this structure which needs four structural parameters to be described. α phase is of the base centered orthorhombic type with two atoms per unit cell. Atomic positions are $(y,-y,-1/4)$ and $(-y,y,1/4)$ in units of the Bravais lattice vectors defined by $(a/2,-b/2,0)$, $(a/2,b/2,0)$ and $(0,0,c)$ in the basis of conventional unit cell vectors. One thus has to determine a, b/a, c/a, and y to fully describe the unit cell.

Experimentally, at room temperature, the parameters are[15] $a=5.39$ a.u., $b/a=2.06$, $c/a=1.73$, and $y=0.105$. The equilibrium volume is $V_0=138.9$ a.u.^{3} Ref. (16).

We calculated the energy-volume curve of the α phase by fully relaxing the structure at constant volume for each point (Fig. 1). From a Birch-Murnaghan fit of this curve one gets $V_0=128.1$ a.u. and $B_0=188$ Gpa. These values are very close to the one obtained with FLAPW[14] but are quite different from experimental values.[16,17] This discrepancy is caused by the limitations of the LDA approximation which underestimates the equilibrium volume and overestimates the bulk modulus. A calculation in the general gradient approximation (GGA) is currently under progress.

To obtain a very good convergence on forces and stress, the four structural parameters have been optimized in a calculation with a constant number of plane waves corresponding to a cutoff energy of about 180 ryd. The atomic volume is then found to be 127.8 a.u.^{3} (corresponding to $a=5.30$ a.u.) and the bulk modulus is 182 GPa. The values we obtain for c/a (1.767) and y (0.107) are very close to the experimental results and to the published calculations, while the b/a value (1.939) is much too small (see Table III). This last point never came up from the previous calculations as this ratio was kept constant. Besides, the conclusions of the experimental study[6] are quite vague. Indeed the variation of b/a and y with pressure are estimated to be smaller than 2%

TABLE II. Equilibrium volumes (V_O in a.u.^{3}) and bulk moduli (in GPa) for the U-fcc, U-bcc, and U-α phases obtained with our plane-wave calculations (PW) compared to FLAPW and experimental results.

	fcc phase		bcc phase		α phase	
	V_0	B_0	V_0	B_0	V_0	B_0
PW (120 ryd)	134.3	154	128.6	170	128.1	188
FLAPW (Ref. 14)	136.5	148			127.9	176
Expt.					138.9 (Ref. 16)	135.5 (Ref. 17)

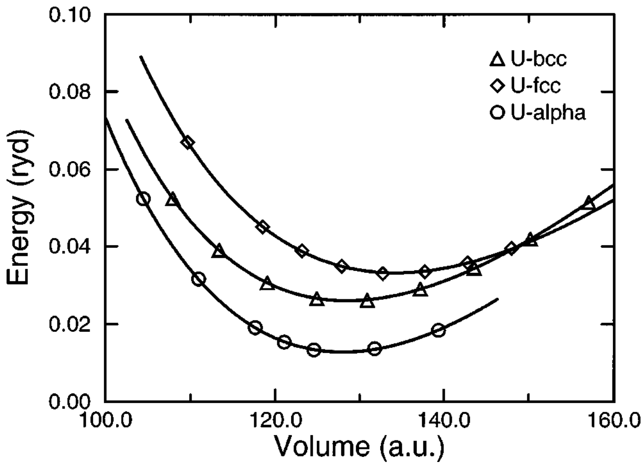

FIG. 1. Variation of the energy of metallic uranium as a function of the atomic volume.

and 5%, respectively. Such variations are claimed to be small and therefore negligible while the c/a variation, regarded as large, is measured to be 3.4% over the same pressure range (see Fig. 2).

D. Structural study of uranium dioxide

We have tested the ability of the uranium pseudopotential to reproduce the bulk properties of uranium dioxide UO_2. Uranium dioxide exhibits the fluorite structure, space group F_{m3m}. There is one formula per unit cell. Uranium atoms form a face centered cubic network, all tetrahedral sites of which are occupied by oxygen atoms. In other words, oxygen atoms form a simple cubic network, half of the cubes (chosen so that they do not share any faces) have in their center a uranium atom. A Troullier-Martins[8] pseudopotential is used to represent oxygen atoms. This pseudopotential has already been used in a former study on zircon.[18] All the calculations on uranium dioxide have been carried out with the PWSCF code. We checked on some test cases that the results obtained with PWSCF and ABINIT codes are extremely close to each other.

We obtain a metallic state for UO_2 while it is experimentally an insulator. It is indeed known that density of states calculations made in the local density approximation lead to a metallic state for UO_2.[19–24] This inability of LDA to reproduce the insulating nature of UO_2 is due to an inaccurate description of electronic correlations and especially of the localized character of uranium f electrons. Using GGA approximation instead of LDA would not restore the insulating character of uranium dioxide as strictly beyond LDA methods, such as LDA+U,[25] are needed to reproduce correctly the electronic characteristics of UO_2.[26,23] As we obtained a metallic state we had to use a sampling grid of the Brillouin zone that contains many k points. The convergence with the number of k points (generated following the Monkhorst and Pack scheme)[27] is given in Table IV. Structural results are given for a $5^3 k$ point grid which has 10 points in the IBZ. A Gaussian spreading of 0.02 ryd is applied. The convergence of the total energy of the UO_2 unit cell with the energy cutoff is given in Table V. For a cutoff of 120 ryd, the variation of energy with volume is given in Fig. 3. From this curve, thanks to a Birch-Murnaghan fit one gets the characteristics indicated in Table VI. One can see that our calculated equilibrium unit cell parameter and bulk modulus are in very good agreement with the results of other LDA calculations based on the all electron LMTO-ASA method.[22,23] The agreement between our pseudopotential calculation and the all electron results proves the validity of our pseudopotential of uranium and its ability to reproduce correctly the properties of UO_2 at the LDA level. Compared to experiments, LDA results are quite correct, the unit cell parameter being 4% too small compared to experiments. We obtain an enthalpy of formation of uranium dioxide from α-uranium and dioxygen of 1058 kJ/mol, which is close from the experi-

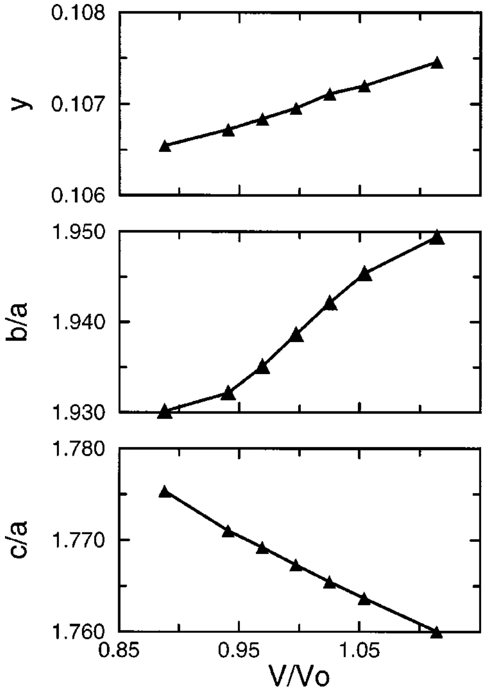

FIG. 2. Variation of c/a, b/a, and y parameters as a function of volume. The volume is normalized to calculated equilibrium volume V_0.

TABLE III. Structural study of the U-α phase. Equilibrium volumes (V_0 in a.u.^{3}), cell parameter (a in a.u.), internal parameters (b/a, c/a, and y), and bulk modulus (B_0 in GPa) for the U-α phases obtained with our plane wave-calculations (PW) using a constant number of plane waves corresponding to a cutoff of about 180 ryd compared to experimental results.

	V_0	a	b/a	c/a	y	B_0
PW (180 ryd)	127.8	5.30	1.939	1.767	0.107	182
Expt.	138.9 (Ref. 16)	5.39 (Ref. 16)	2.06 (Ref. 15)	1.73 (Ref. 15)	0.105 (Ref. 15)	135.5 (Ref. 17)

TABLE IV. Convergence of the total energy E per structural unit as a function of the number of k points for UO_2 fluorite structure. In the first line: number of k points in the Brillouin zone and in the irreducible part of it (between brackets).

Nb of pts	1^3 (1)	2^3 (2)	3^3 (4)	4^3 (10)	5^3 (10)	6^3 (28)
E (ryd)	−107.67864	−107.32347	−107.31688	−107.32083	−107.31997	−107.32099

mental value [1085 kJ/mol (Ref. 28)]. The discrepancy between experimental and calculated values is a bit larger than what one usually obtains in LDA *ab initio* calculations. It comes partly from the inadequacies of LDA in reproducing the electronic structure of UO_2. Using the LDA+U method[23] would partially fill the gap between the calculated and experimental values, the cell parameter being only 2% too small. However, the agreement obtained at the LDA level proves good enough to warrant the relevance of LDA studies of structural properties of uranium dioxide, such as the one on point defects that we present in the following.

III. POINT DEFECTS IN UO_2

A. Point defects configurations

We deal in the following with point defects of UO_2. Isolated vacancies and interstitials of uranium and oxygen have been considered. The study is restricted to neutral defects. We have set aside the important question of the charge state of the defects in UO_2 which has been tackled in former studies using empirical potentials.[1–3] Indeed in the framework of electronic structure methods the charge states of the defects in an insulating material is discussed in terms of the chemical potential of the electrons, i.e., the position of the Fermi level in the insulating gap.[29] Unfortunately, our LDA model of uranium dioxide produces a metallic compound so it is not possible with it to deal with any charged defect. Beyond the discrepancies that may be introduced in our calculated energies and configurations by the error made on the electronic structure, this inability to deal with charged defects turns out to be the main drawback of not using beyond LDA methods. However studying neutral defects is still of great interest as the energy differences between the different charge states of the defects should be negligible compared to the differences between the energies of different kind of defects.

The supercell method has been used. It contains 24 atoms and is made of the repetition, over one of the three axes, of the 12 atom conventional unit cell. The unit cell parameter of this conventional cell has been fixed to 5.24 Å which is the calculated equilibrium value for the bulk. Because of computer limitations, it proved impossible to deal with a cell containing more than 24 atoms. However, in a previous study, Petit *et al.*[4] showed that the size of the supercell has little influence on the calculated energies at least in the unrelaxed configurations. The expected imprecision is of the order of 0.02 eV. The cutoff energy has been kept to 120 ryd. A study of the convergence of the total energy with the size of the k-point mesh and the Gaussian spreading lead us to choose a spreading width of 0.025 ryd for a k-point grid of the Monkhorst and Pack[27] type containing 4^3 points. In the defect free supercell it amounts to 6 k points in the IBZ. The expected imprecision due to the k point grid is about 0.05 eV for total energies. Thus the imprecision on total energies due to the limitations in cutoff energy, supercell size and k point sampling should not be larger than 0.1 eV. The imprecision on formation energies should be smaller as they involve total energy differences.

A specific cell has been built for each type of point defect. To insert a vacancy one simply has to remove an atom of the chosen type from the cell. On the other hand, a choice should be made to insert an interstitial. The uranium interstitial has been put in the center of an empty oxygen cube. For what concerns the oxygen interstitial three distinct insertion sites have been considered: the center of an empty oxygen cube (position O°) and the two positions (O′ and O″) identified by Willis[30] (using neutron diffraction) as being probable positions for the oxygen interstitials. The O′ position is half way from an octahedral site (center of an O_8 cube) and from the line joining two adjacent oxygen atoms. The O″ position lies in the middle of the line joining the octahedral site and a summit of the O_8 cube. It should be noted that for these last two positions (O′ and O″), the number of k points in the IBZ raises from 6 to 10 and 20, respectively.

Atomic relaxation

The energy of the cells have been calculated at fixed atomic positions. Then, as the plane-waves method allows the calculation of forces acting on the atoms, the relaxed atomic configurations have been calculated thanks to a conjugate gradient algorithm. The calculation was carried out until the sum of the forces moduli became smaller than 4.0×10^{-2} ryd/bohr which corresponds to 1.7×10^{-3} ryd/bohr per atom. To estimate the order of magnitude of the imprecision associated with these residual forces, one can associate to them a temperature. Let us consider an atom of mass m, oscillating harmonically at the frequency ν around its equilibrium position. If the point of maximum potential energy (of the order of $1/2^{*}k_bT$) in the oscillation corresponds to a force F one has

TABLE V. Convergence of the total energy E per structural unit as a function of energy cutoff E_c for UO_2 fluorite structure (5^3 k points).

E_c (ryd)	80	100	120	140	160	180
E (ryd)	−107.09887	−107.27191	−107.31997	−107.33535	−107.34056	−107.34180

TABLE VI. Bulk characteristics of UO_2. Comparison between our calculated values of the cell parameter and bulk modulus (first column), the experimental values (second column), and the results of other calculations made using the LMTO-ASA method, within LDA (columns 3 and 4) and LDA+U (column 5).

	PW	Expt.	LDA-LMTO-ASA (Ref. 22)	LDA-LMTO-ASA (Ref. 23)	LDA-U-LMTO-ASA (Ref. 23)
a (Å)	5.24	5.47	5.24	5.20	5.36
B (GPa)	252	207	260		

$$F = 2\pi\upsilon\sqrt{k_B/Tm}. \tag{1}$$

Applying this relation to our case, with a typical frequency of 10^{12} hz for the atomic vibration, one gets, for a force of 1.7×10^{-3} ryd/bohr, a temperature smaller than the room temperature for oxygen as well as for uranium atoms. The precision on the atomic positions is therefore of the order of magnitude of the amplitude of thermal oscillations around the equilibrium position at room temperature, which is quite sufficient. The energy gained during atomic relaxation is indicated in Table VII. It should be kept in mind that the symmetry of the cell has been maintained during the relaxation. This greatly speeds up the calculation but fixes particular directions of relaxations for the atoms, some of them being in fixed positions by symmetry. The small size of the supercell also restricts atomic relaxations. One can see in Table VII that the energy gained through relaxation is very small for oxygen defects. However, atomic displacements are non negligible as they are about 0.14 and 0.06 Å around oxygen vacancy and interstitial (in O° position see below), respectively. At the opposite, energy gain is important for uranium defects. Indeed neglecting this effect leads to an overestimation of the defect energies of about 1 eV which is by far larger than the imprecision due to the calculation uncertainties. Associated atomic displacements are about 0.24 and 0.12 Å for uranium interstitial and vacancy, respectively. Due to computer limitations it was not possible to bring volume relaxation to completion. The energies are thus given at constant supercell volume. Previous calculations[4] performed on the same supercell showed that the volume relaxation was quite small for uranium defects (the unit cell parameter variation was equal to -0.5% for the vacancy and $+3.4\%$ for the interstitial) and completely negligible for oxygen defects.

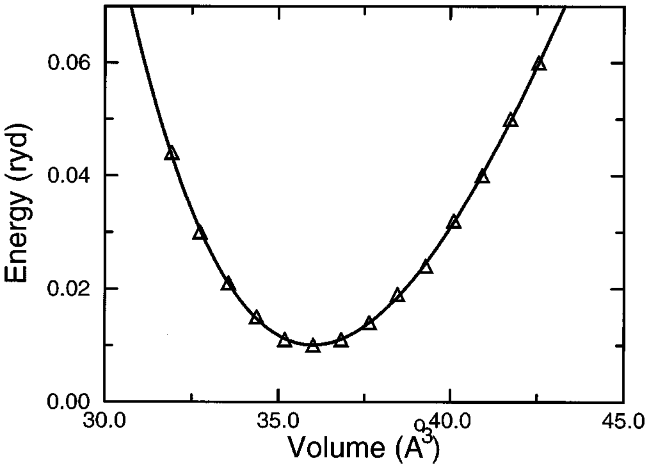

FIG. 3. Variation of the energy of uranium dioxide as a function of the volume of the unit cell.

The oxygen interstitial

Before relaxation the lowest energy position is the central one (O°), O′, and O″ positions being 0.6 and 7.5 eV higher in energy, respectively. During relaxation the interstitial introduced in the O′ position moves and reaches the central (O°) position. In this final configuration the energy is naturally very close to the one of the interstitial initially introduced in the center of the O_8 cube. For what concerns the interstitial in the O″ position, after a few relaxation steps, the energy remains 2.3 eV higher than the one of the central interstitial. Calculations in this configuration being three times longer than the other ones (due to the larger number of k points), we chose not to proceed until complete relaxation, but the last calculated configuration is quite close to the central O° position. One can therefore conclude that the stable oxygen interstitial position for our model is the octahedral position in the center of the O_8 cube and that the other positions are unstable and decay to the central one. It is worth noting that the oxygen interstitial behavior in UO_2 is different from what is observed for α-quartz[31] and zircon.[32] In quartz one gets a peroxide bridge and in zircon it forms a pure dumbbell.

The predicted position is in contradiction with the measurements made by Willis.[30] To explain this discrepancy one should first note that these measurements were made on overstoichiometric oxide. Beside it is known that oxygen interstitials in UO_2 tend to gather and form clusters of defects. Such clusters configurations have not been considered in our calculations (see below).

B. Formation energies of defects

From the calculated total energies one can deduce the energies of the reactions of formation of the point defects. At this point a clear distinction should be made between intrinsic and extrinsic defects. Intrinsic defects are the ones that do not require atoms to be brought to or taken away from the crystal. In the present case they are the Frenkel pairs of each

TABLE VII. Energy gained through relaxation of atomic positions around point defects in UO_2.

	V_O	I_O(O°)	V_U	I_U
Energy gain (eV)	0.027	0.019	1.69	0.64

TABLE VIII. Formation energies of intrinsic point defects in uranium dioxide (units eV). Our values (first column) are compared to LMTO-ASA results (Ref. 4) and experimental estimates.

	Present calc.	LMTO-ASA	Ionic calculation (Ref. 3)	Experimental estimates (Ref. 33)
Oxygen Frenkel pair	3.9	6.7	4.8	3.0–4.6
Uranium Frenkel pair	10.7	30.6	19.4	9.5
Schottky defect	5.8	17.1	11.3	6.0–7.0

atom type, the Schottky defect (two oxygen vacancies and one uranium vacancy) and the complementary defect made of three interstitials that we should name an anti-Schottky defect. These intrinsic defects can also be described as composite as they are the results of combinations of point defects. Such a combination is needed to maintain the relative number of oxygen and uranium atoms. At the opposite elementary defects (vacancies and interstitials) are extrinsic defects. For instance to create an oxygen vacancy without creating at the same time another point defect (uranium vacancy or oxygen interstitial) one has to remove an oxygen atom from the crystal.

Intrinsic defect formation energies

The equations of reaction associated with the formation of intrinsic point defects are

$$\varnothing \leftrightarrow V_O + I_O \quad \text{oxygen Frenkel pair,} \tag{2}$$

$$\varnothing \leftrightarrow V_U + I_U \quad \text{uranium Frenkel pair,} \tag{3}$$

$$\varnothing \leftrightarrow 2V_O + V_U \quad \text{Schottky defect,} \tag{4}$$

$$\varnothing \leftrightarrow 2I_O + I_U \quad \text{anti-Schottky defect.} \tag{5}$$

The last reaction can be expressed as a combination of the three first ones. Thermodynamic quantities associated with this defect can therefore be deduced from the ones calculated for the Frenkel pairs and the Schottky defect. Following the usual definition we considered that the different elementary point defects constituting these composite defects are dissociated. For instance, a Frenkel pair is the result of the creation of a dissociated pair, the vacancy and the interstitial being not interacting with each other.

The free energy of formation of a point defect is defined as the free energy difference between the system with and without the defect,

$$F^F = E^F - TS^F, \tag{6}$$

where E_F and S_F are, respectively, the variation of internal energy and entropy associated with the creation of the defect. Internal energy of formation for each defect can be easily calculated from the energies of the cells: for the Frenkel pairs,

$$E^F_{FP_X} = E^{N-1}_{V_x} + E^{N+1}_{I_x} - 2\times E^N, \tag{7}$$

for the Schottky defect,

$$E^F_S = E^{N-1}_{V_U} + 2\times E^{N-1}_{V_O} - 3\times\frac{N-1}{N}\times E^N; \tag{8}$$

E^N is the calculated energy of the defect free cell; $E^{N\mp1}_{PD}$ is the calculated energy of the cell with the point defect; N denotes the number of atoms in the defect free cell (24 in the present case). The entropy of formation is the variation of vibrational entropy between the defect free and defective crystal. To obtain the exact value of this term, phonon distributions of the perfect and defective cells should be calculated. This calculation is theoretically possible but extremely demanding. Moreover it is known that vibrational entropy of formation is around $2k_B$ in oxides[31] as in metals, which amounts to 0.3 eV at 1000 K. It is therefore reasonable to neglect this small term. We shall, in the following, speak in terms of internal energy rather than free energy.

Applying the formulas given above, one obtains the values indicated in Table VIII for the formation energies of intrinsic point defects in uranium dioxide. Experimental estimates of these formation energies are also given in Table VIII. These are the mostly accepted and recommended values of the experimental formation energies.[33] They come mainly from measurements of self-diffusion coefficients of uranium and oxygen in UO_2 and their interpretation in the framework of the point defect model (see the Discussion section). One could note the good quantitative agreement between plane wave calculated values and experimental estimates.

For comparison we also indicate in Table VIII the values obtained with the LMTO-ASA method[4] and one set of values obtained with interionic empirical potentials using the Mott-Littleton methodology. These last values have been obtained by Jackson[3] using inter-ionic empirical potentials which are based on an ionic description of UO_2 (with formal charges for both ions) and include the effect of ion polarizability through the implementation of a shell model. The other values previously obtained by Catlow[1] using the same kind of model are very close (within 1 eV) to the values of Jackson given in Table VIII. They formed the first sets of calculated values with which it was possible to discuss and rationalize the point defects population in UO_2, using the point defect model (PDM; see below). Nevertheless they overestimate the experimental figures by a factor 2 (except for the oxygen Frenkel pair formation energy) thus preventing their use for a quantitative analysis of the point defect population in uranium dioxide. Such an overestimation is not uncommon when interionic empirical potentials with formal ions charges are used to describe partially covalent oxides.[32] The LMTO-

ASA values are much larger than both our values and the experimental estimates. Despite the better description of electronic structure these figures are not closer to experiment than what one gets with empirical potentials. This is not due to the inability of LMTO methods to take into account atomic relaxations. Indeed we proved that they can only shift formation energies by about 2 eV for uranium defects. The observed overestimation in LMTO-ASA is in fact characteristic of calculation on point defects with this method. Such an effect has already been observed in metals and alloys.[34–36]

Our values thus form the first set of calculated values quantitatively in agreement with the experimental figures.

Extrinsic defect formation energies

The distinction between intrinsic and extrinsic point defects is visible in the equations of reaction of these two kinds of defects. Thus the reaction of formation of the oxygen vacancy is

$$\varnothing \leftrightarrow V_O + \mathrm{O}_{\mathrm{ext}}. \tag{9}$$

It includes the state of the oxygen atom outside uranium dioxide.

To calculate values of the formation energies of extrinsic defects one has to define precisely the state of the atoms outside of the uranium dioxide. Internal energies of formation of extrinsic point defects are then defined as

$$E^{F}_{\binom{V_X}{I_X}} = E^{N\mp 1}_{\binom{V_X}{I_X}} - E^{N}(\pm)E_X. \tag{10}$$

$E^{F}_{\binom{V_X}{I_X}}$ denotes the internal energy of formation of a vacancy or an interstitial of the X species; E^N is the calculated energy of the defect free cell; $E^{N\mp 1}_{\binom{V_X}{I_X}}$ is the calculated energy of the cell with the defect; E_X is the calculated energy of the X element in the chosen reference state.

One of the commonly used conventions is to take as reference an isolated atom infinitely far from the crystal. We did not choose this convention as it raises two problems. First, it is well known that the energy of isolated atoms is very poorly reproduced by LDA calculations. One then introduces an important error in the calculated formation energies which does not come from the system under study but from the chosen reference. Secondly choosing isolated atoms as the reference states comes down to describe an unphysical process of creation of the point defect. Thus an oxygen atom that enters the crystal to form an interstitial (or gets out of it to form a vacancy), does not come from (or go to) a phase made of isolated oxygen atoms. It is true that changing the reference state results only in a shift of the formation energies, but, for the sake of comprehension it is better to choose a reference state that corresponds to a situation that has some physical meaning.

We chose for reference states the elements in their standard states, i.e., dioxygen molecule and α-uranium. One then obtains the energies indicated in Table IX. The formation energy of the oxygen interstitials is found negative. It does not mean that the concentration of oxygen interstitials is infinite. To discuss thermodynamical equilibrium it is necessary to consider the free energies instead of the internal energies. This is especially true for the oxygen phase where the entropy term, driven by pressure, is very important. As we will show different oxygen pressures lead to different formation energies and thus to different defect concentrations. A negative internal formation energy for the oxygen interstitial only means that, strictly speaking in terms of internal energy, an oxygen atom has a lower energy when it is in an interstitial position in $\mathrm{UO_2}$ than in a dioxygen molecule. At 0 K internal and free energies are equal and the negative value of the oxygen interstitial energy is then related to the fact that uranium dioxide spontaneously becomes oxidized in air at temperature as low as 120 °C.[37]

TABLE IX. Internal energies of formation of extrinsic defects in $\mathrm{UO_2}$; reference: elements in their standard states (eV).

	V_O	I_O	V_U	I_U
E_F (eV)	6.7	−2.9	3.3	7.3

The free energy of formation of an extrinsic defect is equal to

$$F^F = F^{N\mp 1} - F^N \pm \mu_X \approx E^{N\mp 1} - E^N \pm \mu_X \tag{11}$$

in the following expression.

F^N and $F^{N\mp 1}$ are the free energies of the crystal with and without the defect. As in the case of extrinsic defect we neglect the vibrational entropy difference between the perfect and defective crystal. The free energies are therefore approximated by the internal ones. μ_X is the free energy of the atom X outside the crystal, i.e., its chemical potential. Specifying the value of this chemical potential comes down to describing the external phase with which the crystal is in equilibrium through exchanges of X type atoms. The existence of this equilibrium forces the chemical potential μ_X to be equal in both phases. On the other hand, for a given temperature and volume, the free energy of $\mathrm{UO_2}$ is uniquely fixed. One then has the relation

$$\mu_U + 2\mu_O = F_{\mathrm{UO_2}} \approx E_{\mathrm{UO_2}}.$$

As long as $\mathrm{UO_2}$ is the only phase under consideration, there is an uncertainty on the values of chemical potentials of U and O. We consider now the equilibrium between uranium dioxide and another phase containing one of the two elements (e.g., X), in a precisely defined state. The existence of this equilibrium ensures that the chemical potential of the X species in the crystal is equal to what it is in the other phase. Specifying the chemical potential of one of the elements then fixes the chemical potential of the other component. In practical conditions uranium dioxide is most of the time in equilibrium with a dioxygen vapor. To specify the chemical potential of oxygen in this vapor one should specify dioxygen partial pressure. One eventually gets a distribution of the formation energies of the point defects as a function of the chemical potential of oxygen or, equivalently, as a function of dioxygen partial pressure. Indeed one has

$$\mu_O=\frac{1}{2}\mu_{O_2}=\frac{1}{2}\left[\mu^0_{O_2}(T)+kT\ln\left(\frac{P_{O_2}}{P^0}\right)\right]$$
$$=\frac{1}{2}\left[E_{O_2}+kT\ln(f(T))+kT\ln\left(\frac{P_{O_2}}{P^0}\right)\right]. \tag{12}$$

The chemical potential in the pressure reference state ($P^0=1$ atm) is the sum of the energy, calculated with the electronic structure code and of the part of the entropy that does not depend on pressure $kT\ln(f(T))$ which amounts for the rotational and vibrational entropy of the dioxygen molecule.[38] This last term varies very rapidly with temperature and is by no means negligible as it amounts to 2.25 eV or 10^{12} atm at 2000 K. Free energies of formation of the point defects are, therefore, for oxygen defects

$$E^F_{\left(\begin{smallmatrix}V_O\\I_O\end{smallmatrix}\right)}=E^{N\mp1}_{\left(\begin{smallmatrix}V_O\\I_O\end{smallmatrix}\right)}-E^N\pm\frac{1}{2}\left[E_{O_2}+kT\ln(f(T))+kT\ln\left(\frac{P_{O_2}}{P^0}\right)\right]. \tag{13}$$

For uranium defects

$$F^F_{\left(\begin{smallmatrix}V_U\\I_U\end{smallmatrix}\right)}=E^{N\mp1}_{\left(\begin{smallmatrix}V_U\\I_U\end{smallmatrix}\right)}-E^N\pm E_{UO_2}\mp\left[E_{O_2}+kT\ln((T))\right.$$
$$\left.+kT\ln\left(\frac{P_{O_2}}{P^0}\right)\right]. \tag{14}$$

The free energies of formation of the defects thus depend on both temperature and the oxygen pressure. For a given temperature there are limits on the oxygen pressure (or oxygen chemical potential) range. One of the limits is that the formation energies of all the defects should be positive to ensure stability of UO_2 with regard to the introduction of defects. It is worth noting that for any oxygen pressure and temperature one has

$$F^F_{FP_X}=F^F_{V_X}+F^F_{I_X} \tag{15}$$

and

$$F^F_S=F^F_{V_U}+2F^F_{V_O}. \tag{16}$$

C. Concentration of the defects in the point defect model

Presentation of the model

The point defect model (PDM) was introduced by Matzke[39,33] and Lidiard[40] to analyze the populations of defects in UO_{2+x}, where x indicates the deviation from stoichiometry. This model is based on the hypothesis that the defects responsible for the deviation from stoichiometry in UO_{2+x} are isolated point defects. Even if it has been known for long that oxygen interstitials form clusters of defects, the PDM is commonly used to analyze the variation of the populations of point defects with stoichiometry or oxygen pressure. It is therefore of great interest to introduce in it the values we calculated for the point defect formation energies. We first present the principles on which the PDM stands and the associated equations.

The PDM is based on the writing of the mass action laws for the reactions of formation of intrinsic defects. The PDM explicitly assumes that the defects are isolated and non interacting. The configurational entropy is simply expressed in terms of concentration by counting the possible defect sites. Point defect concentrations are defined in a lattice model as the number of defects present divided by the number of available sites for the defect under consideration. For the oxygen vacancy there are two possible sites in each unit cell which are the two positions occupied by the oxygen atoms in the defect free crystal. At the opposite all other defects have only one possible site per unit cell, the uranium site for the uranium vacancy and the center of an O_5 cube for the interstitials (see before). Thus in a crystal where there are as many oxygen vacancies as oxygen interstitials, the concentration of oxygen vacancies is twice smaller than the one of interstitials.

To analyze the results obtained with this model one should distinguish two conceptually different regimes: the open one and the closed one, depending on whether uranium oxide can or cannot exchange atoms with the exterior. In the closed regime the numbers of atoms of each type are given thus fixing the deviation from stoichiometry. The only phase under consideration is UO_{2+x}, x being either positive (overstoichiometry) or negative (understoichiometry). At the opposite in the open regime uranium dioxide is in thermodynamical equilibrium with a reservoir with which it can exchange atoms. The deviation from stoichiometry is then a function of the oxygen partial pressure.

Defect concentrations in the closed and open regimes

In the closed regime the equations of the PDM are

$$[V_O][I_O]=\exp\left(-\frac{E^F_{FP_O}}{k_BT}\right), \tag{17}$$

$$[V_U][I_U]=\exp\left(-\frac{E^F_{FP_U}}{k_{BT}}\right), \tag{18}$$

$$[V_O]^2[V_U]=\exp\left(-\frac{E^F_S}{k_BT}\right). \tag{19}$$

A supplementary equation is given by the definition of the deviation from stoichiometry in UO_{2+x}. A counting of the number of atoms on each site gives at first order

$$2[V_U]+[I_O]=2[I_U]+2[V_O]+x. \tag{20}$$

With these four equations it is possible, for a given value of x, to calculate the concentrations of the point defects at any temperature.

In the open regime the concentrations of defects are expressed as functions of the temperature and the dioxygen partial pressure. For instance the oxygen vacancies concentration is

$$[V_O]=\exp\left(-\frac{\left(E_{V_O}^{N-1}-E^{N}+\frac{1}{2}\mu_{\mathrm{O}_2}\right)}{kT}\right)$$

$$=\exp\left(-\frac{E_{V_O}^{F}}{kT}\right)(P_{\mathrm{O}_2}f(T))^{-1/2}. \qquad (21)$$

From Eq. (21), similar expressions can be obtained for the other point defects using Eq. (17) to Eq. (19).

Traditional analysis of the PDM

It is experimentally known that oxygen defects dominate over the uranium defects in UO_2 at any temperature and stoichiometry. From this observation, in the framework of the PDM, one traditionally assumes that the over (respectively under) stoichiometry is accommodated by oxygen interstitials (respectively vacancies). This leads to the following.

Understoichiometry $(x<0)$. The dominant defect is the oxygen vacancy:

$$[V_O]=-\frac{x}{2}. \qquad (22)$$

Stoichiometry $(x=0)$. The intrinsic disorder is of the anion Frenkel type:

$$[I_O]=2[V_O]=\sqrt{2}\,\exp\left(-\frac{\beta}{2}E_{FP_O}^{F}\right). \qquad (23)$$

Overstoichiometry $(x>0)$ The overstoichiometry is accommodated by oxygen interstitials:

$$[I_O]=x. \qquad (24)$$

One can draw some graphs to illustrate these three regimes. We chose for the formation energies typical values of 3.0 eV for $E_{FP_O}^F$, 6.2 eV for E_S^F, and 9.2 eV for $E_{FP_U}^F$. These values are in the range of commonly accepted values indicated in Table VIII.[33] 3.0 eV is the first estimate made for the oxygen Frenkel pair formation energy.[39] The oxygen pressure (or oxygen chemical potential) range is limited. A first limit corresponds to the fact that the concentrations of all point defects should be smaller than 1. Using activation energies measurements for self-diffusion of U and O one gets 6.2 eV for E_S^F and 9.2 eV for $E_{FP_U}^F$ (see below). Choosing arbitrarily a temperature of 1700 K one gets the variation of concentrations with stoichiometry indicated in Fig. 4. The three regimes are clearly visible: under stoichiometry with x fixing the oxygen vacancy concentration, the nearly stoichiometric regime where oxygen Frenkel pairs dominate and the over stoichiometry regime with x fixing the oxygen interstitial concentration. In the open regime the oxygen partial pressure is given by Eq. (21).

D. Analysis of the PDM with our calculated values

We applied the PDM with the values we calculated for the intrinsic point defects formation energies (Table VIII). As can be seen in Fig. 5 the three regimes are different from the traditional analysis and can be characterized as follows.

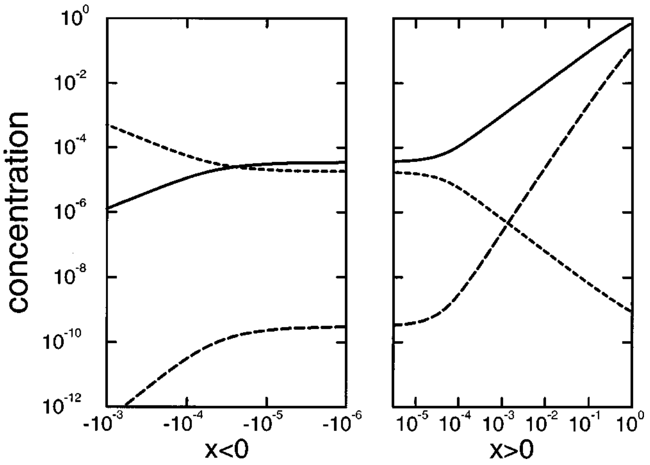

FIG. 4. Traditional analysis of the point defect model. Variation of the concentrations of point defects with the deviation from stoichiometry: understoichiometric regime (on the left) and overstoichiometric regime (on the right). Full (respectively dotted and dashed) lines indicate the concentration in oxygen interstitial (respectively oxygen vacancy and uranium vacancy). The concentration of uranium interstitial is negligible. $T=1700$ K; $E_{FP_O}^F=3.0$ eV; $E_S^F=6.2$ eV; $E_{FP_U}^F=9.2$ eV.

Understoichiometry $(x<0)$. The dominant defect is the oxygen vacancy. It accommodates the deviation from stoichiometry:

$$[V_O]=-\frac{x}{2}. \qquad (25)$$

Stoichiometry $(x=0)$:

$$[I_O]=[V_O]=[V_U]. \qquad (26)$$

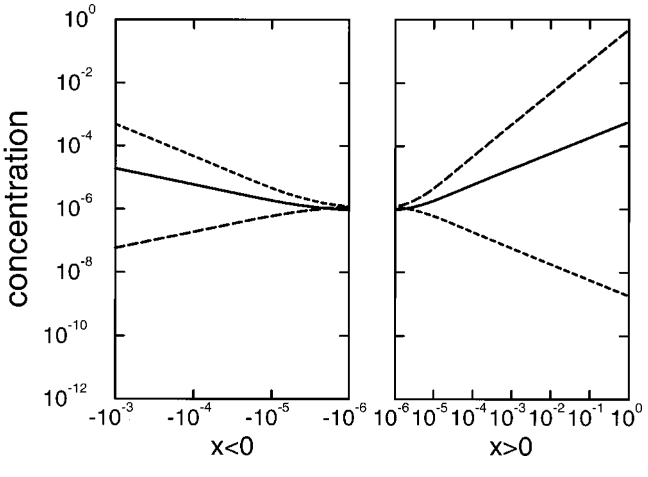

FIG. 5. Analysis of the point defect model with our calculated values of the intrinsic point defect formation energies. Variation of the concentrations of point defects with the deviation from stoichiometry: understoichiometric regime (on the left) and overstoichiometric regime (on the right). Full (respectively dotted and dashed) line indicate the concentration in oxygen interstitial (respectively oxygen vacancy and uranium vacancy). The concentration of uranium interstitial is negligible. $T=1700$ K; $E_{FP_O}^F=3.9$ eV; $E_S^F=5.8$ eV; $E_{FP_U}^F=10.7$ eV.

TABLE X. An example of the population of defects obtained with the point defect model using the calculated energies of formation of defects. $T=1700\,\mathrm{K}$.

Regime	x	$[I_O]$	$[V_O]$	$[V_U]$	$[I_U]$
Understoichiometry	-0.02	2.2×10^{-10}	0.01	1.6×10^{-14}	9.6×10^{-20}
Stoichiometry	0	1.5×10^{-6}	1.5×10^{-6}	7.4×10^{-7}	2.1×10^{-27}
Overstoichiometry	0.04	2.5×10^{-4}	9.1×10^{-9}	0.02	7.9×10^{-32}

There is no dominant defect. There are twice more oxygen vacancies than oxygen interstitials. The perfect stoichiometry is restored by the presence of many uranium vacancies.

Overstoichiometry ($x>0$). The dominant defect is the uranium vacancy. It accommodates the deviation from stoichiometry:

$$[V_U]=\frac{x}{2}. \tag{27}$$

A numerical application at $T=1700\,\mathrm{K}$ is given in Table X.

In the open regime the concentration of point defects and the deviation from stoichiometry as a function of oxygen partial pressure are indicated in Fig. 6. The oxygen pressure (or oxygen chemical potential) range is limited. A first limit corresponds to the fact that the concentrations of all point defects should be smaller than 1. For 1700 K the oxygen partial pressure should therefore range between 10^{-24} and 10^{-9} atm. Moreover for an oxygen chemical potential smaller than -5.4 eV, it becomes thermodynamically favorable to dissociate UO_2 in α-uranium and dioxygen. This raises the minimum of oxygen pressure to 4×10^{-18} atm (at 1700 K).

It can be noted that for any stoichiometry the concentration in uranium interstitials is negligible. On the other hand, our values of the formation energies lead to a dominant role of the uranium vacancy for the overstoichiometric oxide which is in contradiction with the experimental facts. The PDM, used with the energies we calculate, do not reproduce the fact that oxygen defects are dominant for all stoichiometry.

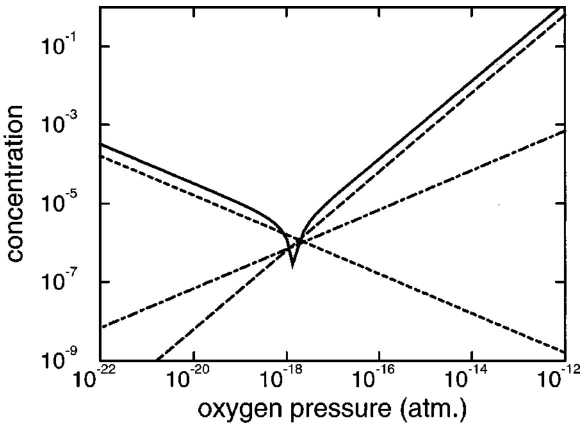

FIG. 6. Concentration of point defects in UO_2 and stoichiometry as a function of dioxygen partial pressure in the open regime with our calculated values. $T=1700\,\mathrm{K}$; $E^F_{FP_O}=3.9\,\mathrm{eV}$; $E^F_S=5.8\,\mathrm{eV}$; $E^F_{FP_U}=10.7\,\mathrm{eV}$.

E. Discussion

Condition of applicability of the PDM

To ensure that the PDM reproduces the fact that oxygen defects are dominant for all stoichiometries, some conditions should be fulfilled by the point defect formation energies. Indeed oxygen Frenkel pairs should be favored against other intrinsic defects (uranium Frenkel pairs or Schottky defects). This implies

$$E^F_{FP_O} \ll E^F_{FP_U} \tag{28}$$

and

$$\frac{E^F_{FP_O}}{2} \ll \frac{E^F_S}{3}. \tag{29}$$

The first condition raises no question and is always verified. The second condition is less obvious. Should the case where $E^F_{FP_O}/2 \gg E^F_S/3$ arise, oxygen vacancies in the stoichiometric oxide would be mainly due to the Schottky defects and in the overstoichiometry would be accommodated by uranium vacancies. Therefore, with such a ratio between $E^F_{FP_O}$ and E^F_S, the PDM cannot be directly applied.

The previously published calculations (empirical potentials and LMTO-ASA) respect both of the above conditions and they are coherent with the PDM analysis of the predominance of oxygen defects. Unfortunately the discrepancies between the values they predict and the experimental estimates make questionable the conclusions obtained with these values.

With our values one gets $E^F_{FP_O}/2=1.95\,\mathrm{eV}$ and $E^F_S/3=1.97\,\mathrm{eV}$. It is therefore quite normal that for a stoichiometric compound, our values lead to the presence of the three kinds of defects (oxygen vacancies and interstitials and uranium vacancies) in the stoichiometric oxide and to the dominant role of uranium vacancy in the overstoichiometric oxide.

Experimental situation

From the experimental point of view many estimates exist for the formation energy of oxygen Frenkel pair. Values of 3.5 eV,[33] 3.7 eV,[41] 4,1 eV,[42] 4.6 eV,[43] and 5.8 eV (Ref. 44) have been proposed. The activation energies for the self-diffusion of oxygen and uranium have been measured for various stoichiometries. From the PDM equations and making the assumption that oxygen point defects are dominant, one can deduce, from the measured formation energy of the Frenkel pair and self diffusion activation energies, estimated values of the formation energies of the other intrinsic defects (Schottky and uranium Frenkel pair). The values given by Matzke in Ref. 33 and indicated in Table VIII have been obtained following this reasoning. More precisely to obtain an estimate of the Schottky defect formation energy one writes the activation energy for uranium self-diffusion in stoichiometric UO_2 as the sum of the effective formation energy of uranium vacancy and its migration energy:

$$E_U^{act}=E_S^F-E_{FP_O}^F+E_{V_U}^M. \tag{30}$$

With figures taken from Ref. 33: $E_{FP_O}^F=3.0$ eV, $E_{V_U}^M=2.4$ eV, $E_U^{act}=5.6$ eV, one gets $E_S^F=6.2$ eV. The relation $E_{FP_O}^F/2 \ll E_S^F/3$ is then fulfilled and the values from Ref. 33 obtained using the PDM are coherent with it.

But a great uncertainty remains on the different experimental values that enter Eq. (30). For instance one can take $E_{FP_O}^F=4.6$ eV (Ref. 43) and $E_U^{act}=4.4$ eV.[45] Equation (30) then leads to $E_S^F=6.8$ eV.

One then has $E_{FP_O}^F/2 \gg E_S^F/3$ which is in contradiction with the hypothesis under which Eq. (30) can be used. From the last set of values one cannot deduce any value for E_S^F.

In this last case the PDM cannot be applied to get coherent values of the formation energies. It proves therefore unable to describe properly the defects populations. The uncertainty that remains on the experimental values of energies for the oxygen Frenkel pair formation and for self-diffusion activations is such that one cannot decide whether the PDM can or cannot properly describe defects concentrations in UO_2 and their variation with stoichiometry.

Weakness of the PDM

The main weakness of the PDM is the central assumption that the point defects are isolated and do not form clusters. It is indeed known to be untrue especially for oxygen interstitials that form the so-called Willis clusters.[30] Even if this weakness is well known the PDM remains very popular as it is indeed very difficult to take into account explicitly the defect clusters. Indeed the calculation of the formation energies of these objects lead to quite heavy calculations that cannot be achieved at present with electronic structure methods. Moreover, these objects are uneasy to deal with, from the conceptual point of view, for what concerns their configurational entropy for instance.

Nevertheless we saw that the uncertainty on the experimental values are such that one cannot decide whether the PDM can be applied or not. However, the values we calculate tend to indicate that one has to explicitly consider the defects clusters (especially the one formed by oxygen interstitials) to be able to construct a model that can satisfactorily describe the populations of defects as a function of stoichiometry. Taking such clusters into account should lead to a decrease of the formation energies of the oxygen defects and should restore the fact that oxygen defects are preponderant at all stoichiometries.

IV. CONCLUSION

A study of the point defects in UO_2 in the DFT-LDA framework using the plane wave pseudopotential method has been realized. As a prerequisite to this study, a pseudopotential to describe the uranium element has been generated with the Troullier-Martins method. A structural study of different metallic uranium phases and uranium dioxide fluorite structure was performed to check its validity. A particular attention has been paid to the uranium α phase which is the stable one at ambient conditions. The variation of the structural parameters (a, b/a, c/a, and y) with pressure has been considered. Variation of y and c/a are in very good agreement with experiments. The b/a ratio, the variation of which had not been studied in previous calculations, is underestimated by 6%.

Tackling the study of point defects in UO_2, we considered the four elementary point defects: vacancies and interstitials of uranium and oxygen atoms. Their atomic configurations and energies have been calculated using a 24 atoms supercell. The importance of atomic relaxations for uranium defects has been shown. The calculated values of point defects formation energies fit very well the experimental estimates. They constitute the first set of formation energies for the isolated point defects in UO_2 coherent with experimental figures. An analysis of these values in the framework of the point defect model commonly used to analyze the population of defects in uranium dioxide leads to a dominating role of uranium vacancies in the overstoichiometric oxide in contradiction with experimental facts. An analysis of the PDM shows that its applicability relies on the ratio of oxygen Frenkel pair and Schottky trio formation energies. The uncertainty on the experimental values is such that one cannot decide on the applicability of the PDM. Our calculated values indicate that one should probably go beyond a model of isolated species to obtain a satisfactory description of the population of defects in UO_2 and the way the deviations from stoichiometry are accommodated by this material.

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*Email address: jpcrocombette@cea.fr

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