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Influence of charge states on energies of point defects and clusters in uranium dioxide

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The variation of formation energies of point defects and clusters in uranium dioxide (UO_2) as a function of their charge states is studied by density functional theory (DFT). Di- and trivacancies are considered as well as various assemblies of oxygen interstitials, namely the cuboctahedral defect (either empty or filled) and the split-di-interstitial. The energies of formation of these defects for various possible charge states are calculated using the DFT + U approach. The occurrence of multiple minima is circumvented by the use of the U-ramping technique [Meredig *et al.*, Phys. Rev. B **82**, 195128 (2010)]. One finds that point defects and vacancy clusters bear their formal charges, deduced from the ionic picture of bonding in UO_2. Conversely, clusters of oxygen interstitials are much less charged than this fully ionic limit. The energy gain upon clustering is vastly modified when the possible charge of defects is taken into account. Vacancy clusters prove only marginally stable compared to their isolated counterparts. Clusters of oxygen interstitials are found energetically unstable with respect to isolated interstitials in the stoichiometric compound.

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I. INTRODUCTION

Uranium dioxide is a key material for the nuclear industry. It is indeed the usual fuel for pressurized water reactors. Atomic defects are of key importance for several properties of UO_2. They drive diffusion properties, provide insertion sites for fission products, and accommodate stoichiometry variations. The last two properties involve not only point defects but also their clusters. Indeed, some fission products are thought to be preferentially accommodated in clusters of vacancies,[1] while oxygen interstitials are expected to aggregate into clusters in the oxygen hyperstoichiometric oxide.[2]

It is well known that in semiconductors or insulators, point defects and clusters may bear a charge. Indeed, the ionic picture of bonding in UO_2, namely the idea that bonding in UO_2 comes mainly from the attraction of U^{4+} and O^{2-} ions, naturally suggests that point defects are charged; the expected charges of oxygen and uranium defects being +2 for the oxygen vacancy, −2 for the oxygen interstitial, −4 for the uranium vacancy, and +4 for the uranium interstitial. Such formal charges are assumed in the so-called point defect model,[3] which relates the deviations from stoichiometry in uranium dioxide to the concentrations of point defects and the concentrations of electronic defects. The empirical potentials used to describe UO_2 are also based on the interactions between oxygen and uranium ions. When such potentials are used to describe atomic defects, these defects are naturally considered to be charged.

Recent atomic scale simulations on defects in UO_2 use density functional theory (DFT) to describe the chemical interatomic bonding. In such works, the possible charge of the point defects and clusters is generally overlooked (see references below). For instance, no study exists to our knowledge about the possible charge states of any cluster in UO_2. In the same way, almost all calculations on point defects neglect their possible charge, the only exception we are aware of being the recent works by Nerikar *et al.*,[4] Crocombette *et al.*,[5] and Andersson *et al.*,[6] which all show that point defects are indeed charged in UO_2. The reason for neglecting the charge of defects may originate from the fact that initial DFT studies used a simple functional either in the local density approximation (LDA)[7,8] or the generalized gradient approximation (GGA).[9] With these functionals, the insulating nature of UO_2 cannot be reproduced, and it comes out as a metal (while it is in fact a Mott–Hubbard insulator[10]). In such calculations, it is therefore impossible to deal with the possible charge of defects. This initial weakness may have pushed/oriented the community into neglecting this possible charge of defects in studies using more advanced beyond-LDA methods even when these methods were able to reproduce the fact that UO_2 is an insulator.

Going beyond the few studies mentioned above on point defects, we extend, in this paper, the study of charge of defects to point defect clusters. We use DFT simulations within the so-called DFT + U framework.[11] We show that the energetic properties of cluster formations are vastly modified when their charge is taken into account, which has a great impact on their stability with respect to point defects.

This paper is organized as follows. In the next section, we present the methodology of our simulations. Sec. III will present our results for the formation energies of point defects and clusters as well as the thermodynamically relevant clustering energies of point defects into clusters. In that section, we shall also compare our results with the ones available in literature (mainly on neutral defects). The final section will be devoted to discussions focused mainly on the impact of charge of defects on clustering.

II. METHODOLOGY

A. Technicalities

The calculations were performed in the DFT framework using the projector augmented wave (PAW) method as implemented in the ABINIT[12–14] code. The suitable PAW atomic data were generated using the ATOM-PAW[12] tool. The cutoff energy used for all the calculations was 20 Ha, while the energy cutoff for the fine fast Fourier transform grid was set to 30 Ha.

For noncorrelated electrons, the Perdew–Burke–Ernzerhof functional[13] within GGA was used. In order to account for the strong correlations that exists between uranium f electrons, a so-called DFT + U term was added for these electrons. The full rotationally invariant formulation of Liechtenstein *et al.*[14] was used with the full localized limit procedure to remove double counting[15] as implemented in ABINIT.[16] The value of U is specified below. The spin-orbit interaction was not taken into account since it is commonly neglected in calculations of point defects in UO_2. We use a supercell approach to calculate defect properties. The defect free supercell is a $2 \times 2 \times 2$ repetition of the conventional cubic cell of UO_2, thus containing 96 atoms. Due to computational limitations we used only the Γ point to sample the Brillouin zone of the supercell, which corresponds to an unshifted $2 \times 2 \times 2$ k-point sampling in the conventional cell. The calculations are performed at constant volume, corresponding to a conventional 12-atom cell of 5.51-Å side, which is the equilibrium lattice constant for our calculations (to be compared to the experimental value of 5.47 Å[17]).

Experimentally, the magnetic and crystallographic structure of UO_2 varies with temperature. At noncryogenic temperatures, uranium oxide is paramagnetic with a perfect fluorite structure. UO_2 exhibits a first-order phase transition at $T_N = 30.8$ K to a transverse antiferromagnetic (AF) state[18] accompanied by a Jahn–Teller (JT) distortion of the oxygen sublattice.[19] The AF structure has long been believed to be $1k$, but it proves in fact to be $3k$.[20]

In calculations on defects, the magnetic structure is always simplified to its $1k$ approximant (though bulk calculations on the $3k$ structure exist[21]). Most calculations investigate only the fluorite structure. Some of the most recent studies compare the results obtained for the fluorite and the JT distorted structure.[6,22] In such calculations, the symmetries induced by the atomic structure and the AF ordering are preserved in the calculations, so many more symmetries are applied for the fluorite structure than for the JT distorted structure, which proves much less symmetric due to the atomic displacements.

We chose another approach. First, we chose not to investigate the JT distortion and to place the atoms in the symmetric fluorite positions. By doing so, we aim to compare our results with experimental data obtained at temperatures very far from the Neel transition. Second, as paramagnetism cannot be reproduced in the small cells we are dealing with, we considered, as others, the $1k$ AF ordering. We believe such calculations to be observed as paramagnetism than as diamagnetic (no magnetism at all) calculations. Finally, even if the atomic structure is symmetric, we turned off any symmetrization of the electronic structure, thus allowing complete freedom on the electronic wave function. Doing so, we lift the symmetry constraints that exist on electronic structure in calculations with full fluorite symmetry. We believe that such calculations offer the best (though only approximate) description of the atomic and electronic structure of UO_2 at temperatures larger than 30 K.

B. Multiple minima problem

The DFT + U approach introduces an orbital dependant Hamiltonian so that the calculation may converge to different points depending on the initial occupations of the density matrix of f electrons.[23] The errors due to this multiple minima problem are quite large. It may rise up to about a few tenths of eV per formula unit in the case of UO_2.[21,22] The occurrence of multiple minima probably spoiled many former calculations on defects in UO_2 (see the analysis by Dorrado *et al.*[22] and Crocombette *et al.*[5]). This difficulty is now acknowledged by the community doing calculations on UO_2.[5,6,23,24] For lack of a theoretical solution to solve the multiple minima problem analytically, one has to resort to tricks to reach the real minimum of the calculation, i.e. the true ground state. The most exact way is the brute force approach which consists in testing all possible density matrix occupations to find the ones leading to the lowest energy.[24,25] However, this method is intractable in practice for defects as one would have to test different occupation matrices for uranium first, second, etc., neighbors of the defects. Geng *et al.*[24] recently proposed a quantum-annealing approach which includes adding atomic distortions of vanishing intensity to reach the true ground state. This approach seems promising. However, little information is given about its practical implementation, and it seems to require huge calculation times. As a compromise, we chose to use the U-ramping method recently proposed by Meredig *et al.*[26] In this method, one starts from a standard LDA or GGA calculation, then one slowly increases the value of the U and J parameters that appear in the DFT + U formalism.

Our calculations are performed in practice in the following way: the structure of the supercell is relaxed within GGA down to forces lower than 0.05 eV/Å. A ramping calculation is then performed at constant geometry with the possible additional charge. The ramping starts from a simple GGA calculation, then the U and J parameters of DFT + U are increased in 25 steps following an arithmetic sequence from zero up to their maximum values of 4.5 eV for U and 0.5 eV for J. For each step of the sequence, the calculation is restarted from the density and wave function files of the previous step. In the last calculation, the atomic structure is relaxed again down to forces lower than 0.02 eV/Å. We use this procedure for the defective boxes as well as for the defect-free supercell, the energy of which enters the definition of the formation energy of defects. As acknowledged by their authors[26] and observed by others,[24] the U-ramping method does not work perfectly, as low-lying metastable states may be reached instead of the absolute ground state in calculations on perfect UO_2. However, the error remains very small (Meredig *et al.*[26] find an error of 15 meV per formula unit in the case of UO_2). With such calculations, we obtain a gap in the electronic structure of 2.74 eV, which is larger than the experimental value of 2.1 eV.[17] However, this discrepancy does not come from the U-ramping procedure but is due to a too-loose sampling of the Brillouin zone.[24] Unfortunately, it was not possible to consider a tighter mesh beyond the Γ point, due to limits in computational resources.

C. Defects under study

As far as point defects are concerned, we dealt with the oxygen vacancy and interstitial and the uranium vacancy. The uranium interstitial was not considered. For the clusters of defects, we focused on clusters of vacancies and clusters of oxygen interstitials. The mixed divacancy ($V_U V_O$), made of an oxygen vacancy neighboring an uranium vacancy, was investigated, as well as the trivacancy ($V_U 2V_O$), made of the association of two oxygen-vacancy first neighbors to an uranium vacancy. For this last cluster, three different arrangements of the two oxygen vacancies are possible. They can be first, second, or third neighbors, with oxygen atoms missing at the opposite sides of the edge, face, and body of the cube containing the uranium vacancy. This corresponds to (100), (110), and (111) directions for the line joining the two oxygen vacancies.

Various structures of clusters of oxygen interstitials were also calculated. We investigated here some of the clusters proposed and calculated in literature.[27,28] First, we considered the cuboctahedral defect in which the cube formed by eight oxygen atoms is replaced by 12 oxygen atoms forming a cuboctahedron. It was found[27] that this cuboctahedron can be either empty (COTv) or filled with an additional oxygen interstitial (COTo) [see Fig. 1(a)], thus amounting to four and five oxygen interstitials, respectively. Finally, we considered the so-called split-di-interstitials with three oxygen interstitials surrounding one oxygen vacancy [see Fig. 1(b)]. This cluster was found by Geng *et al.* to be the stable form of 2:2:2 and 3:3:2 Willis clusters and noted V-$3O''$.[27] The same structure was found independently by Andersson *et al.*[28] and noted IX2. We arbitrarily choose this last notation for this cluster. All these defects can bear a charge. In reality, this means that the overall charge inside a volume that includes the defect is not zero. The usual way, which we follow in this paper, to deal with such charged defects within supercell calculations, is to add or remove electrons in the supercell containing the defects. For each defect, we contemplated various possible charge states based on the formal charges of uranium and oxygen ions in UO_2, namely U^{4+} and O^{2-}. For point defects and oxygen clusters, all possible charge states between the neutral to the fully formally charged defect were investigated. For vacancy clusters, a wide range of charges was also considered, namely 0 to -4 for V_UV_O and 1 to -2 for V_U2V_O.

For each defect, one then has to perform a different calculation for each possible charge state (following the procedure described above). One eventually obtains the energies and structures of the boxes containing the defects in their various possible charge states. The atomic structures of the clusters prove to depend lightly on their charge. The relaxed supercells containing the COTo (charge -2) and the IX2 charge (-3) clusters are given in Fig. 1.

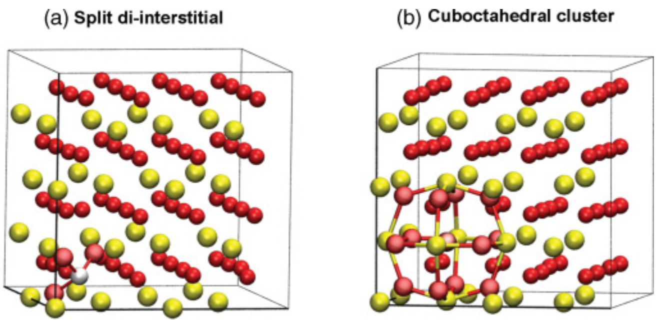

FIG. 1. (Color online) Clusters of oxygen interstitials. The entire supercells are represented. Yellow (light grey in print) and red (black in print) spheres indicate regular uranium and oxygen atoms, respectively. Left panel: split di-interstitial (IX2) with a -3 charge; three oxygen atom (pink/dark grey in print) share and empty oxygen site (indicated by a white sphere). Right panel: cuboctahedral (COTo) cluster with -2 charge; 12 oxygen atom (pink/light grey in print) form a cuboctahedron, the center of which (bright pink/bright grey in print sphere) is either occupied (COTo) or empty (COTv).

D. Formation energies of defects

From the energy of the box containing the defect (Def) in a specific charge (q), its formation energy can be calculated as follows:

$$E^{\text{form.}}_{\text{Def}^q} = E^{N+n_U,2N+n_O}_{\text{Def}^q} - (N+n_U)E_U - (2N+n_O)E_O + q\varepsilon_F + \text{corr.} \quad (1)$$

where:

(i) $E^{N+n_U,2N+n_O}_{\text{Def}^q}$ is the energy of the box containing the defect, with $N+n_U$ uranium atoms and $2N+n_O$ oxygen atoms, N being the number of formula units in the perfect supercell (i.e. $N=32$). Here, n_O and n_U can in principle be either positive or negative, which corresponds to adding or removing atoms, respectively. In this paper, as only vacancies are considered for the uranium specie, n_U is always negative.

(ii) q is the charge of the defect, ε_F is the Fermi energy, and corr. stands for corrections to be applied on charged calculations (see below).

(iii) E_U and E_O are the reference energies for uranium and oxygen atoms, respectively. We chose to give the formation energies in the so-called oxygen-rich conditions, where the reference for oxygen is the oxygen molecule so that:

$$E_O = 1/2E_{O_2}. \quad (2)$$

In practice the energy of the di-oxygen molecule was calculated by imposing seven electrons up and five electrons down for the 12 electrons of the 2s shells of the two oxygen atoms. This procedure is needed to ensure the convergence of the calculation to the triplet paramagnetic state, which is the ground state of the oxygen molecule.

The reference energy for uranium must then follows from:

$$E_U = \frac{E^{N,2N}}{N} - 2E_O = E_{UO_2} - E_{O_2} \quad (3)$$

where $E^{N,2N}$ is the energy of the defect-free supercell.

One may then rewrite the formation energy of defects as a function of the energies of di-oxygen and the defect-free box:

$$E^{\text{form.}}_{\text{Def}^q} = E^{N+n_U,2N+n_O}_{\text{Def}^q} - \frac{(N+n_U)}{N}E^{N,2N} + (n_U - n_0/2)E_{O_2} + q\varepsilon_F + \text{corr.} \quad (4)$$

Note that it is legitimate to choose other references for oxygen and uranium energy. For instance, one could choose for E_U the energy of bulk uranium, but then the reference energy of oxygen should be deduced from Eq. (3) and not chosen as $\frac{1}{2}$ $E(O_2)$. Choosing, in the formation energies of defects, oxygen and uranium energy references to be equal to di-oxygen molecule and bulk uranium, respectively, would be inconsistent from the thermodynamical point of view. It would lead to errors in the formation energies of defects involving both oxygen and uranium atoms (for instance clusters of vacancies). These errors would scale as the formation energy of the UO_2 compounds from its pure element counterpart and amount to dozens of eV.

We now turn to the last two terms of the formation energies [Eqs. (1) and (4)], which appear for charged defects only. The first one, which involves the charge of the defect and the Fermi level of the material, counts the energy gained or lost in the charging process.[29] The last term of Eqs. (1) and (4) denotes the corrections that should be introduced in charged supercell calculations to remove the spurious interaction of the defect with its periodically repeated images. We follow the procedure recently set up by Taylor *et al.*[30] for the correction on the energy of the supercell and the associated potential shift.

One finally obtains for charged defects a formation energy which varies linearly with the Fermi level. In insulators, the Fermi level can, in principle, lie anywhere between the top of the valence band and the bottom of the conduction band. In the next section, we therefore present the results for formation energies as graphs, giving the energy as a function of the position of the Fermi level between the top of the valence band (chosen as the zero of energy for the Fermi level) and the gap of the material (2.74 eV). The special case of pure stoichiometric UO_2 is discussed in Sec. III.B.

III. RESULTS

A. Formation and reaction energies as a function of the Fermi level

1. Formation energies of single defects

The formation energies of point defects (V_O, I_O, and V_U) are presented in Fig. 2. For the oxygen vacancy case, the three lines corresponding to the three charge states contemplated are explicitly drawn (see the upper panel of Fig. 2). For a given position of the Fermi level, the most stable charge state is the one whose formation energy is the lowest. One can see that, for the Fermi level going from the valence to the conduction band, it changes from +2 to +1 and eventually zero charge. In the other figures, only the minimum in energy will be drawn with changes in slopes corresponding to changes in charge states of minimum energy, as indicated by the steplike curves.

As described above, V_O tends to be positive. Conversely, I_O and V_U tend to be negative. These signs of the charges are consistent with the ionic picture which predicts V_O to be +2, I_O to be −2, and V_U to be −4. These formal charges are indeed the most stable ones for a wide range of Fermi levels, but some other charge states prove possible.

The formation energies of the vacancy clusters under study are shown in Fig. 3. Note that V_U2V_O being a stoichiometric defect, its formation energy does not depend on the chosen references. As far as the V_U-V_O divacancy is concerned, the most stable charge state is −2 for most Fermi levels. This is consistent with a fully ionic picture, which suggests the association of +2 oxygen and −4 uranium vacancies. In the same way, the trivacancies prove neutral for all Fermi levels except the ones very close to the band edges. Considering the three possible structures of a trivacancy, we find that the most stable one has two oxygen-vacancy second neighbors to each other [vacancies aligned along (110)].

For point defects and vacancy clusters, the ionic picture seems therefore to work rather well; in the sense that, for the majority of Fermi levels, the most stable states do have the charge deduced by the ionic picture. One can see, however, that other stable charge states may appear when the Fermi level deviates from midgap. More positive (negative) charge states prove more stable when the Fermi level is close to the valence (conduction) band.

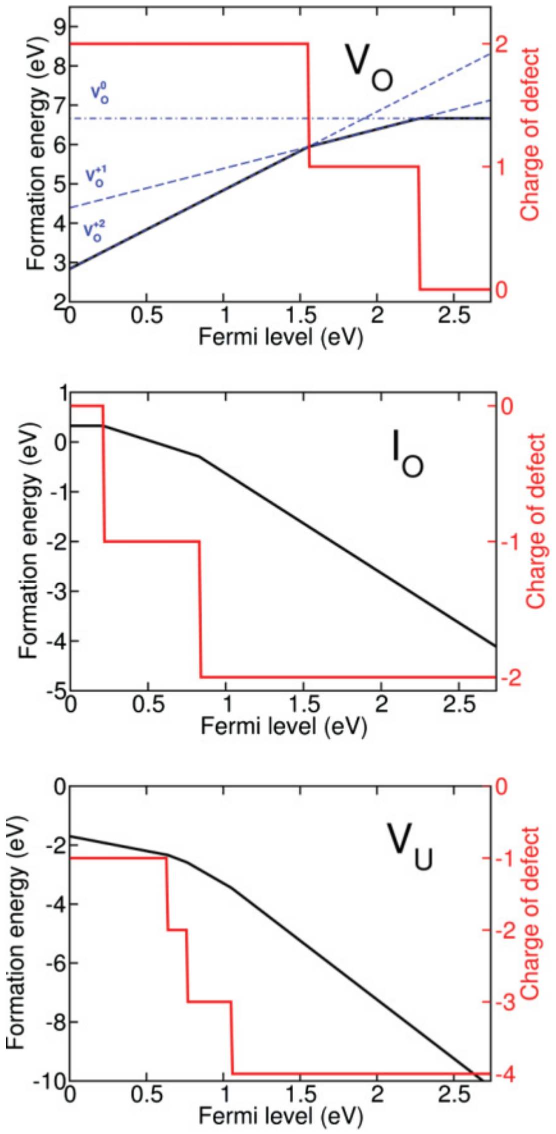

FIG. 2. (Color online) Formation energies (broken lines, left scale) and most stable charge states (step lines, right scale) of oxygen vacancies (top), oxygen interstitials (middle), and uranium vacancies (bottom) as a function of the Fermi level in oxygen-rich conditions. In the case of oxygen vacancies, three lines corresponding to 0, +1, and +2 charge states are drawn, while for the other defects, only the minimum in energy is indicated.

The formation energies per additional oxygen atom and the charge states of the oxygen interstitial clusters are plotted in Fig. 4. It is worth noting that, for all clusters, the charge step by step decreases from zero to their formal ionic charges. This leads to very high charges down to −10 for the COTo cluster. However, such formal charges are reached only for Fermi levels quite close to the conduction band, while for intermediate values of ε_F, the charge is around half of the fully ionic limit. Therefore, for such clusters, assuming fully charged configurations would lead to severe overestimation

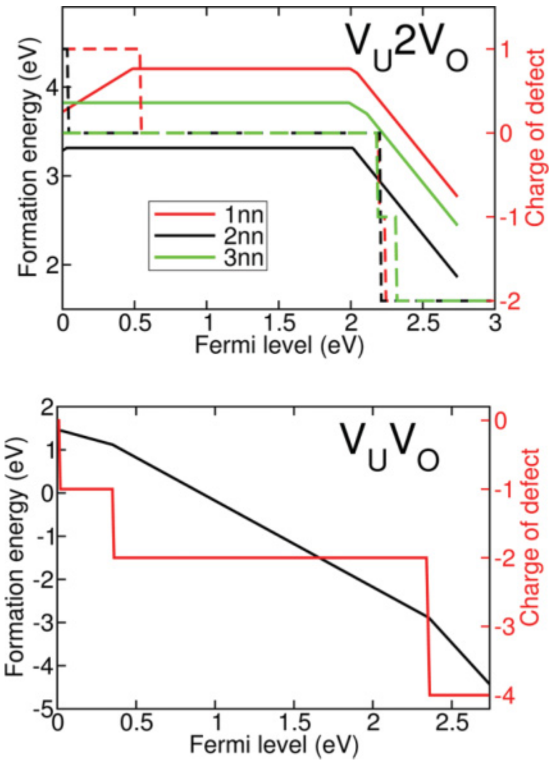

FIG. 3. (Color online) Formation energies (broken lines, left scale) and most stable charge states (step lines, right scale) of vacancy clusters, in oxygen-rich conditions for $V_U V_O$ (see the text).

of the charges (and energies) for most positions of the Fermi level. The formation energies per interstitial of the various oxygen clusters appear rather close to each other. However, the COTo cluster proves to be the most stable for all values of ε_F. Conversely, the COTv and IX2 relative stability changes with the position of the Fermi level.

2. *Formation energies of composite intrinsic point defects*

The previous section dealt with extrinsic defects, the creation of which involves the addition or removal of atoms from the crystal. In this section, we combine the formation energies of extrinsic point defects to discuss the formation energies of intrinsic defects, which are the ones that do not require atoms to be brought to or taken away from the crystal. In this paper, we have access to the formation energies of the oxygen Frenkel pair and the Schottky trio. These intrinsic defects are the results of combinations of point defects which correspond to the following reactions:

$$\emptyset \rightarrow I_O + V_O \tag{5}$$

for the oxygen Frenkel pair and

$$\emptyset \rightarrow V_U + 2V_O \tag{6}$$

for the Schottky trio.

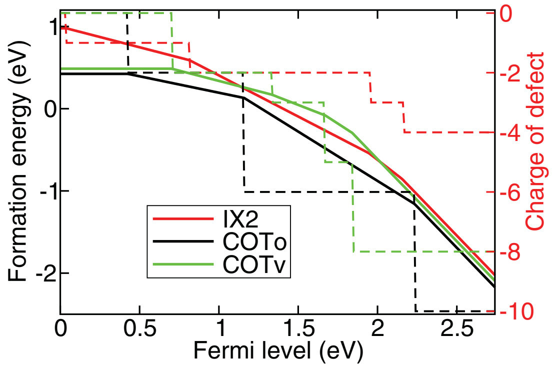

FIG. 4. (Color online) Formation energies per additional oxygen atom (broken lines, left scale) and most stable charge states (step lines, right scale) of clusters of oxygen interstitials in oxygen-rich conditions.

The formation energies of these defects are the sum of the formation energies of their constituents. As they do not involve adding or removing atoms from the crystal, they prove not to depend on the energy references for U and O. The charge and energy of the constituents of the composite defects vary with the Fermi level, and so does the formation energy of the composite defects. The formation energies of an oxygen Frenkel pair and a Schottky trio are indicated in Fig. 5 together with a comparison of neutral calculations.

3. *Clustering of defects*

The energy of clustering of vacancies corresponds to the following reactions:

$$V_U + V_O \rightarrow V_U V_O \tag{7}$$

$$V_U V_O + V_O \rightarrow V_U 2V_O. \tag{8}$$

The clustering energy will be negative when the energy is gained in the clustering reaction.[31] As in the case of composite defects, these energies depend on the position of the Fermi level. For the clusters of oxygen interstitials, we choose to plot the clustering energy per additional oxygen atom, which allows direct comparison between them. The lines indicating the clustering energies (see Fig. 6) exhibit many changes in their slopes when the Fermi level varies from the valence to the conduction band. Indeed, such a break appears each time

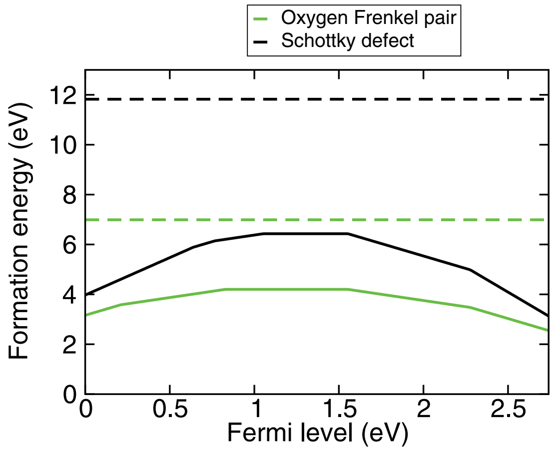

FIG. 5. (Color online) Formation energies of the oxygen Frenkel pair and the Schottky defect. Solid lines indicate charged calculations. Results of neutral calculations (broken lines) are given for comparison

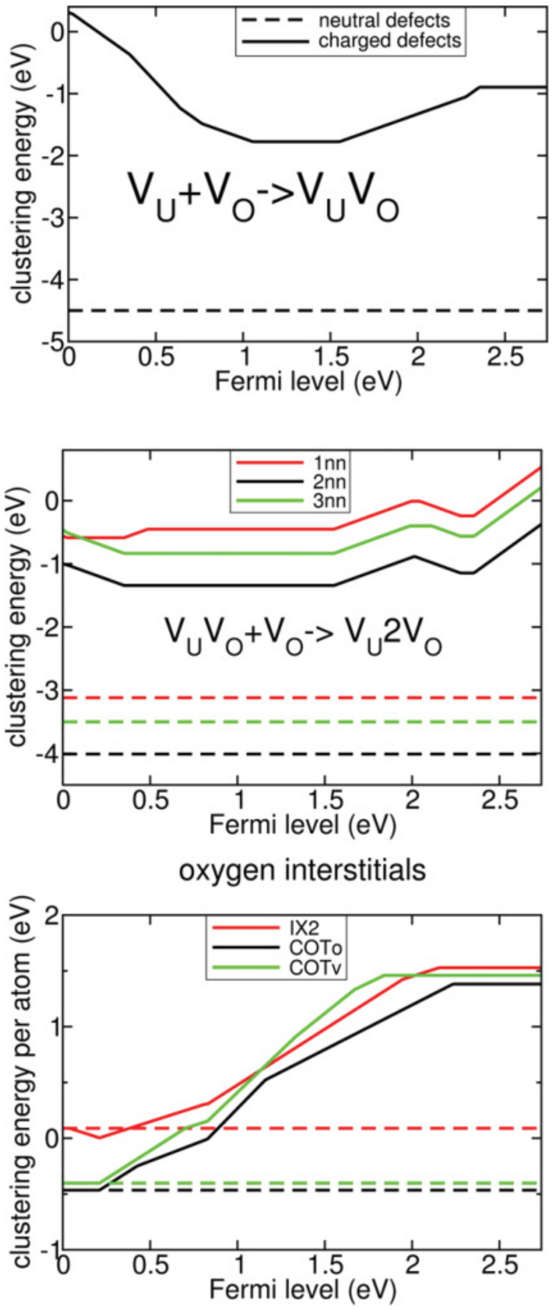

FIG. 6. (Color online) Clustering energies of the vacancy and oxygen interstitial clusters. Solid lines indicate charged calculations. Results of neutral calculations (broken lines) are given for comparison.

the charge of any defect appearing in the reaction equation experiences a change in its charge state.

The clustering of vacancies proves energetically favorable. However, the energy gains upon clustering decrease close to the band edges. This is due to the large decrease of the formation energies of charged configurations of the uranium (oxygen) vacancies close to the conduction (valence) band. This large decrease is less marked for vacancy clusters which have lower charges than the sum of the charge of their isolated counterparts.

Conversely, for clusters of oxygen interstitials, the energy of clustering proves to increase continuously when ε_F goes from the valence to the conduction band. Starting from negative values, indicating energy gain upon clustering, it swiftly becomes positive, which indicates that the association of oxygen interstitials becomes more and more energetically unfavorable.

B. Energies for pure and stoichiometric UO_2

1. *Position of the Fermi level and associated energies*

In the previous sections, energy results were given as a function of the Fermi level. One could wish to specify the position of the Fermi level in order to deal with numbers and not curves. However, the exact point in the gap where the Fermi level lies is not obvious. In principle, it cannot be deduced from the energetics of the defects presented above. Indeed, it may vary with the impurity content or with self doping by the defects themselves. Things are simpler when one deals with the ideal case of pure and stoichiometric UO_2 in thermodynamic equilibrium. UO_2 is then an intrinsic semiconductor, meaning that the position of the Fermi level is given by the equilibrium of electrons in the conduction band and holes in the valence band. Neglecting the very small shift that may appear due to the curvature of the valence and conduction band,[32] one can consider for all practical purposes that ε_F lies at the middle of the gap (i.e. $\varepsilon_F = 1.36$ eV in our simulations). Indeed, the energy of the gap being smaller than the formation energy of oxygen Frenkel pairs or Schottky defects (with a $2/3$ factor on this last energy to account for the fact that Schottky defects involve three point defects), the dominant disorder for stoichiometric UO_2 is the electron-hole pair. Electrons and holes are thus the majority species, and they are in equal concentrations to ensure charge neutrality. This is realized when the Fermi level is positioned at midgap. Taking into account the defect clusters does not change the picture as their concentrations, at thermal equilibrium for stoichiometric UO_2 for any temperature of interest, are lower than the ones of point defects (either for energetic or configurational entropy reasons).

The Fermi level being at midgap, it is possible to specify the charges of the various defects and to give figures for their formation energies (see Table I). The corresponding formation energies of composite defects and clustering energies are given in Table II. One can note that, in the stoichiometric UO_2, point defects and vacancy clusters bear their formal charges while the oxygen interstitial clusters are less charged than expected from the ionic picture.

TABLE I. Charge and formation energies of point defects and clusters in pure stoichiometric UO_2. The energies are given with an oxygen molecule reference (oxygen rich conditions).

Defect	I_O	V_O	V_U	V_U2V_O	V_UV_O	IX2	COTv	COTo
Charge	−2	2	−4	0	−2	−2	−3	−6
Ef (eV)	−1.4	5.6	−4.7	4.2/3.3/3.8	−0.9	−1.0	−1.7	−3.4

TABLE II. Formation energies of composite defects and clustering energies in pure stoichiometric UO_2.

Formation energies (eV)	FPO	Sch	$V_U 2V_O$	Clustering energies (eV)	$V_U + V_O \rightarrow V_U V_O$	$V_U V_O + V_O \rightarrow V_U 2V_O$	$4^* I_O \rightarrow$ COTv (per at.)	$5^* I_O \rightarrow$ COTo (per at.)	$2I_O \rightarrow$ IX2 (per at.)
Exp.[35,40]	3.0–4.6	6.0–7.0							
Charged calculations									
This paper	4.2	6.4	4.2/3.3/3.8		−1.8	−0.5/−1.3/−0.8	1.0	0.7	0.9
Nerikar *et al.*[4]	2.7								
Crocombette *et al.*[5]	4.8								
Andersson *et al.*[6] no JT	3.1/3.3/3.4	5.0/6.0/6.4			−0.4/−1.2/−1.2				
Andersson *et al.*[6] JT	4.1/4.3/4.1	6.8/7.7/7.1			−0.9/−1.5/−1.3				
Neutral calculations									
This paper	7.0	11.8	4.2/3.3/3.8		−4.5	−3.1/−4.0/−3.5	−0.4	−0.5	0.1
Dorrado *et al.*[22] JT/no JT	6.5/5.8								
Andersson *et al.*[6] JT/no JT	6.4/5.3	12.0/10.2	4.6/5.5		−2.9/−3.4				−0.2
Crocombette *et al.*[5]	6.4	9.9							
Geng *et al.*[26,35,39]	5.4	10.6	5.0				0.4	−0.3	0.2
Brillant *et al.*[36]					−0.8				
Thompson *et al.*[37]			4.1/3.3/3.5						

2. *Comparison with literature for point defects*

The figures given in Table II allow the comparison of our results with results from the literature. Such comparison can only be qualitative, as many differences exist between the various studies. These include the choices of simulation codes but also the choices for atomic and electronic symmetries and the treatment of the multiple minima problem.

We focus first on the neutral oxygen Frenkel pair for which many calculated values are available in literature. Recent analysis by Crocombette *et al.*[5] and Dorado *et al.*[22] of published results show that many of them are quite probably spoiled either by the absence of DFT + U corrections[8,9] or by the likely occurrence of multiple minima.[4,32–34] All these calculations give spuriously small values. Thus, we focus on recent calculations which take into account the possible occurrence of metastable states. Our formation energy of the neutral Frenkel pair is of the same order of magnitude but slightly larger than the results obtained by Dorado *et al.*,[22] Andersson *et al.*,[6] Geng *et al.*,[33] and Crocombette *et al.*[5] The first two sets of results were obtained with symmetries turned on. The authors considered either the full fluorite symmetry ("no JT" in the table) or only the ones preserved after introduction of the JT distortion ("JT" in the table). Geng *et al.*'s[33] calculations do not include symmetry either on atomic positions or on wave functions, but use LDA and not GGA as all other calculations do. Finally, the last calculation by Crocombette *et al.*[5] was performed with the same approach for the symmetry as in this paper (fluorite structure no symmetrization of the wave functions) but with a different theoretical framework [local hybrid gunctional for correlated electrons (LHFCE) [34] and not DFT + U]. In view of differences between the various calculation choices, we do not know if this slightly larger value in our calculations for the formation energy of the oxygen Frenkel pair is significant. Nevertheless, we are confident it does not come from a multiple minima problem, as this phenomenon is usually of larger amplitude in the bulk energy and should thus lead to an underestimation of the energy of formation of defects (as in older calculations).

Much fewer results are available for oxygen Frenkel pairs made of charged point defects (V_O^{+2} and I_O^{-2}). Nerikar *et al.*'s[4] calculated value of the formation energy quite certainly suffers from a multiple minima problem. Crocombette *et al.*[5] give a slightly larger value than the present result. Andersson *et al.*[6] give two sets of three different values (see Table II). In these two sets, the first figure is for uncorrected calculations, i.e. without the corrections on charged calculations that appear in Eq. (1); the second is corrected, and the last one is for two distant defects in the same cell. Unfortunately, the corrections for charged defects are not identical between our calculations and theirs. Comparing uncorrected values, we find our figure (3.8 eV) to lie in between their two uncorrected figures, while our corrected value is on the higher side of their bracket.

Beyond these comparisons, with previous calculations, the most important point is that our value for charged defects fits nicely in the experimental bracket,[35] while the energy of neutral Frenkel pairs are much larger than experiments. This is quite reassuring for the validity of our simulations and confirms that point defects are indeed charged in UO_2.

Turning now to the Schottky trio, again, the most important point is that our charged result is in good agreement with the experimental bracket,[35] while our neutral result is close to the ones available in literature. The only available results for charged defects ($V_U^{4-} + 2V_O^{2+}$) are on the ones by Andersson *et al.*[6] Our uncorrected value (4.4 eV) proves larger than the comparable values by Andersson *et al.*, while our corrected value falls in between their two sets of values.

To summarize on point defects, our values are on the larger side of the spread observed in literature, but for charged defects, they fall nicely within experimental brackets.

3. *Comparison with literature for defect clusters*

Clusters of defects have been less studied than point defects. However, some results are available to compare with our results. We find the $V_U V_O$ divacancy to be -2 in stoichiometric UO_2 with a clustering energy of -1.8 eV. The same charge is contemplated by Andersson *et al.*[6] They find, as we do, that charged divacancies are more stable than neutral ones. Our clustering energy values are not far but larger than theirs. This may be the consequence of the aforementioned difference in the formation energies of oxygen Frenkel pairs. The value of Brillant *et al.*[36] for neutral calculations seems to suffer from a multiple minima problem.

For trivacancies, one does not need to care about charges, as these defects are neutral for stoichiometric UO_2. Our values for the formation energies compare very well with the results given by Thompson *et al.*,[37] using the same ramping method to avoid the multiple minima problem. They indeed find very close energies and the same ordering in energy for the various arrangements of the two oxygen vacancies. In the works by Geng *et al.*[24] and Andersson *et al.*,[6] the structure of the trivacancies are not specified. Andersson *et al.* does not give formation energies, but they can be deduced. Both studies thus lead to results comparable to ours but slightly larger.

We are not aware of literature results on charged clusters of oxygen interstitials but only of results for neutral configurations. Geng *et al.*[27,38] considered the same clusters as we did, while Andersson *et al.*[28] focused on IX2 only. Our neutral results agree with these previous results on the fact that COTo clustering is favorable, and IX2 clustering is unfavorable. However, we find COTv to be stable, while Geng *et al.* find it unstable.

IV. DISCUSSION

In view of our results and the comparison with other works, the first thing to note is that the U-ramping method appears to work well. Indeed, our values for formation and reaction energies are close to the ones obtained with quantum annealing or density matrix occupation control. For instance, one does not observe in our results the very small formation energies of point defects which indicate a wrong ground state for the defect-free bulk. Moreover, the closeness of our results on trivacancies with the ones obtained by Thompson *et al.*[37] shows that the U-ramping method leads to reproducible results, which is very satisfactory. The remaining small differences probably come from the different codes used in their calculations (VASP) and ours (ABINIT).

Turning now to the importance of considering charged defects, it appears clearly that formation energies can deviate strongly from the values obtained for the neutral configurations when charge is considered. Correspondingly, the most stable charge state is very often not the neutral configuration. Thus, concerning point defects, our calculations confirm what was already obtained by others,[4–6] namely that point defects in UO_2 are charged. We find them to bear their formal charges, i.e. I_O^{2-}, V_O^{2+}, and V_U^{4-} in the stoichiometric material. Moreover, our calculations show that clusters in UO_2 are charged, too. As indicated above, we evidence that vacancy clusters bear their formal charges, while oxygen interstitial assemblies are much less charged than expected from the ionic limit (Table I). Such incomplete charging of the oxygen clusters probably comes from the fact that the ionic limit predicts huge charges (-4, -8, and -10 for IX2, COTv, and COTo, respectively). Such large accumulation of charge in a very small space induces a strong repulsion, which destabilizes the highly charged clusters.

The deviations of formation energies between charged and neutral calculations have a huge impact on the formation energies of composite defects and on the clustering energies; see the comparisons between charged and neutral calculations in Figs. 5 and 6 and the numbers in Table I. For both the oxygen Frenkel pair and the Schottky trio, the formation energy is divided by about two when charged defects are considered. As far as vacancy clusters are concerned, it appears that the energy gained in the clustering process is largely overestimated by neutral calculations. Clustering energies amount to 0 to -2 eV for charged defects, while it ranks from -3 to -5 eV for neutral configurations. Even more importantly, for oxygen interstitial clusters, taking into account the charge of defects leads to a different qualitative conclusion than the one obtained by neutral calculations. Indeed, while clustering is favorable for neutral configurations, it shifts from favorable to hugely unfavorable for the Fermi level going from valence to conduction band.

The origin of the observed stabilization of charged defects vs their neutral configurations and the interest of writing the formation energies as a function of the value of the Fermi level can be illustrated on the oxygen Frenkel pair case. It will also allow us to highlight the shortcomings of neutral calculations. UO_2 being a rather ionic compound, oxygen ions tend to be -2. Neutral calculations of the oxygen Frenkel pair are based on adding an oxygen atom in a supercell while removing the same atom in another supercell. As the oxygen specie has a strong electronegativity, the oxygen interstitial wants to attract two electrons. In a neutral calculation, these electrons must come from the supercell containing the interstitial, and indeed it was found in literature[39] that a neutral oxygen interstitial bears in fact -2 charge with two uranium in the box experiencing a change of charge from $+4$ to $+5$. In the same way, a neutral oxygen vacancy repels two electrons and introduces two U^{3+} uranium ions in the simulation box.[39] The cost of creating these wrongly charged U^{3+} and U^{5+} ions in neutral calculations explains why the formation energy of an FP made of oxygen atoms is higher than the one of an FP made of oxygen ions. Indeed, if one performs charged calculations with $+2$ charge for the vacancy box and -2 charge for the interstitial box, one in fact reproduces the addition of an O^{2-} ion in a box and its removal in another one. In such calculations, the charge of the displaced oxygen ion is preserved in the process, and there is no need to transfer electrons locally to or from surrounding uranium ions. To rephrase it, neutral calculations force the charge compensation to proceed locally, both in the interstitial and vacancy supercell. On the contrary, in charged calculations, the charge compensation is global, the -2 interstitial equilibrating the $+2$ vacancy. Moreover, writing the formation energies of charged defects as a function of the position of the Fermi level allows extending the above reasoning to isolated defects. Indeed, electrons and holes (or U^{3+} and U^{5+} in an ionic picture) exist in excess in the material with respect to atomic defects. The charging of the defects can thus proceed at the expense of such equilibrium electrons or holes. The energetic cost of these charges is given by the Fermi level, which is the chemical potential of electrons.

Considering the clusters of defects, as in the case of point defects, charging leads to a decrease in their formation energies (see Figs. 2 and 3). Nevertheless, their formation at the expense of point defects is much less favorable when the charge of defects is considered. For vacancies, the overestimation of the binding of clusters in neutral calculations comes from the fact that vacancy clusters are in fact less charged than their isolated constituents. The overestimation of the energies made in neutral calculations is thus larger for isolated vacancies than for clusters. This spuriously enlarges the clustering energy in neutral calculations. The same reasoning applies for assemblies of oxygen interstitials. Indeed, such clusters being less charged than suggested by the ionic limit, their energy in neutral calculation is relatively less overestimated than for isolated interstitials.

Finally, having investigated the possible charge of clusters, we obtain of new picture on their stability. Our calculations show that vacancy clusters are only marginally stable compared to isolated vacancies. They are thus expected to be minority in the material due to configurational entropy, which favors disconnected defects. For assemblies of oxygen interstitials, the situation is even more drastic, as such clusters prove energetically unstable in UO_2. One can thus expect them to be in negligible amount even in the case of a supersaturation of oxygen interstitials, e.g. under irradiation.

V. CONCLUSION

In this paper, we studied the charge of point defects and clusters in UO_2. We showed that the charging of defects induces huge effects on their formation energies as well as on their clustering energies. Point defects and vacancy clusters bear their formal charges, while assemblies of oxygen interstitials are less charged than expected in the ionic limit. As a consequence, the ionic picture of bonding in UO_2 does not work perfectly to predict the charge of defects. A complete search as the one we did, investigating all possible charge states and their energies as a function of Fermi level, should thus be performed, especially when new kinds of defects are considered.

From the calculated energies, we deduced, first, that vacancy clusters have a small binding energy and will be minority in the material due to entropy reason. Second, oxygen interstitial clusters prove energetically unstable in the stoichiometric material and are thus expected to be in negligible amount, even in the case of supersaturation of oxygen defects.

Finally, the charge of defects and clusters are expected to play a role in other aspects of their behavior. For instance, diffusion properties through migration energies, as well as energetics of fission products, are expected to be affected by the charge of defects.

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