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First principles modelling of oxygen impurities in UN nuclear fuels

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ABSTRACT

We report results of first principles VASP supercell calculations of O impurity in UN fuels placed either at an interstitial tetrahedral position or as a substitution for a host N ion. In the latter case O perfectly fits into N site producing no lattice distortion. Such the O substitutional impurity only slightly affects the formation energies of U and N vacancies nearby. In both interstitial and substitutional positions O atom attracts the additional electron density and transforms into the negatively charged ion. Oxygen incorporation into pre-existing N vacancy is energetically more favourable than into the interstitial position. The O impurities produce an additional peak at the low energy side of N contribution to the DOS calculated for uranium mononitride which could be used for the O identification by means of the UPS spectroscopy. We compare also the DOS calculated for UN and hypothetical isostructural UO. Both O solution and incorporation energies are negative, indicating that O penetration into UN fuel is the energetically favourable. The migration energy of the interstitial O ion is estimated as 2.8 eV.

1. Introduction

Along with fundamental interest in properties of heavy f-elements, studies of actinides and their compounds are considerably stimulated by their nuclear applications. In particular, *nitrides* (especially, UN) are of special interest as advanced nuclear fuels and targets for fast reactors and for transmutation of Pu and minor actinides [1]. However, metal nitrides demonstrate high reactivity with oxygen, their oxidation can affect the fuel fabrication process, its performance and safety. Despite several experimental studies for ZrN oxidation [2–4], very little is done for UN and the nitride oxidation mechanisms in general [5].

First experimental studies of O in UN were performed by Matzke in 80s [1]. This activity was recently continued at ITU combining several techniques [6–8]. Along with these experimental studies, a series of the first principles calculations of pure UN was published very recently [9–14] whereas a few studies [15–17] focused on intrinsic defects (U and N vacancies) present in UN at different concentrations. In order to shed light on the UN fuel oxidation, in this paper we discuss the results of the first principles study of O impurities.

2. Theoretical

The uranium mononitride (UN) has rock-salt (f.c.c.) structure. The O impurities can either substitute for host N ions (Fig. 1(b)) or occupy an interstitial position (Fig. 1(c)). Along with these two static configurations, we studied also *migration* of O impurities (Fig. 1(d) and analysed how the O atom substituting for a host N ion affects the U and N vacancy formation energies. For this purpose, we used mostly two types of supercells having different size, built by expanding the translation vectors of the primitive cell by 3 × 3 × 3 (54 atoms) [O substitutional impurity] and 4 × 4 × 4 (128 atoms) [interstitial O atom]. After analysis of the perfect UN properties, we placed O atoms in these supercells which corresponds to the defect concentration of 3.7% and 16%, respectively. In the calculations we optimised both the local atomic structure (geometry) around a defect, as well as the lattice parameter.

We used the DFT computer code VASP 4.6 [18,19] using formalism of Projector-Augmented-Wave (PAW) method including the plane-wave basis set. We use the Perdew-Wang-91 GGA non-local exchange-correlation functional [20] and the scalar relativistic PAW pseudopotentials representing the core electrons of U (with $6s^26p^66d^25f^27s^2$ valence shell), N ($2s^22p^3$) and O ($2s^22p^4$) atoms (containing 14, 5 and 6 valence electrons, respectively). The plane-wave cut-off energy is chosen to be 400 eV. The Monkhorst–Pack scheme [21] for 3 × 3 × 3 *k*-point mesh in the Brillouin zone was employed. The topological (Bader) atomic effective charges were calculated following procedure [22]. In all calculations the spin polarisation of UN with defects has been taken into account.

3. Main results

Before making periodic defect calculations, we tested how properties of a pure UN depend on the supercell size.

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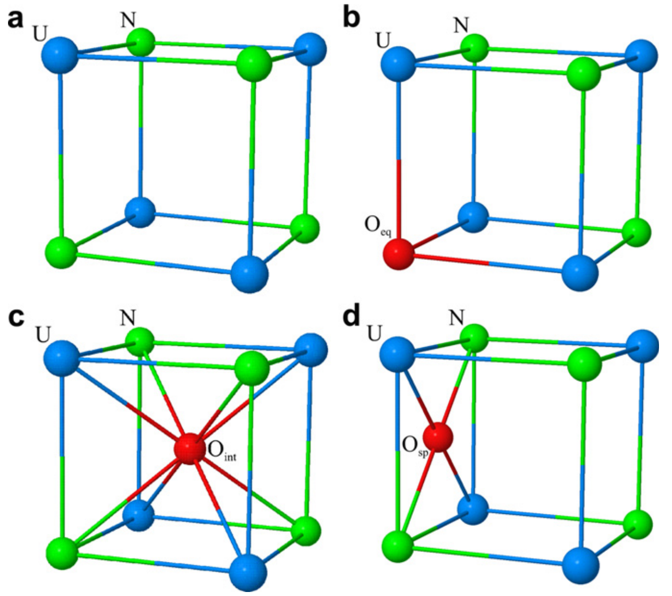

Fig. 1. The perfect UN cell (a), O atom substituting host N ion (b), the interstitial O atom (c), its migration along the (001) direction (d).

The conclusion could be drawn from Table 1 that the properties do not depend practically of the supercells size, the unit cell of two atoms reproduces quite well experimental lattice constant and cohesive energy. Notice also a considerable deviation of the effective charges from formal charges ±3 e caused by essential contribution of the covalency in the U–N chemical bonding due to U 5f,6d and N 2p atomic function hybridisation.

3.1. Substitutional O impurity

3.1.1. The atomic structure and energetics

Defect energetics could be characterized by the incorporation (I), relaxation (R), and solution (S) energies, as it was suggested for the first time by Grimes and Catlow in the shell model calculations for He in UO_2 [23]:

$$I = E_{\rm def} - (E_{\rm vac} + E_{\rm O}), \tag{1}$$

where $E_{\rm def}$ is the (negative) total energy of the supercell with a defect (O impurity occupying N vacancy), $E_{\rm vac}$ supercell with a N vacancy, and $E_{\rm O}$ O atom in the ground triplet state at infinity. Negative I value means that the incorporation process is energetically favourable. The relaxation energy is the difference between the total energy of the supercell with a defect calculated for unrelaxed and relaxed lattice (all atoms are allowed to move to the energy minimum), this is always positive (or close to zero). The solution energy takes into account the energy cost for creation of the N vacancy in a perfect crystal,

$$S = I + E_{\rm f}, \tag{2}$$

Where the (positive) vacancy formation energy is

$$E_{\rm f} = (E_{\rm vac} + E_{\rm N}) - mE_{\rm coh}, \tag{3}$$

with $E_{\rm N}$ energy of N atom at infinity and $E_{\rm coh}$ the cohesive energy per unit cell multiplied by a number of unit cells in the supercell (27 in our case). The formation energy for a N vacancy is 9.1 eV (taking into account the relaxation energy of 0.7 eV); for U vacancy this energy equals to 9.4 eV (with the relaxation energy of 1.0 eV) [15,16]. In the equilibrium position ionic relaxation around defects has very local character; only the nearest neighbour (NN) atoms around the defect are displaced, while these displacements are quite small, especially for the $V_{\rm N}$ (0.03 Å). This is accompanied by the local charge redistribution; practically a whole charge of a missing N atom (−1.6 e) is localized on six NN U ions. In the case of $V_{\rm U}$ the local perturbation range is a little larger.

Table 1
Basic properties of the perfect UN crystal calculated using different supercells

Atoms in supercell	Effective charge, e	Cohesive energy, eV	Lattice constant, A
2	1.66	14.65 (expt 13.6)	4.854 (expt 4.886[1])
16	1.65	14.63	4.852
54	1.65	14.63	4.850
250	1.63	14.63	4.850

Table 2 summarizes results of our calculations. The O incorporation energy is quite negative, whereas the solution energy remains slightly negative. That is, even with a formation of the N vacancy (necessary for placing therein O atom) it is still energetically favourable, O atom penetration into UN bulk. However, taking into account necessity of the preliminary O_2 bond breaking in a gas phase (5.12 eV), only formation of interstitial O atom turns out to be energetically favourable (See Table 3).

Second, the O atom substituting a host N ions fits into a lattice very comfortably, making no local distortion (the relaxation energy is zero, the nearest atom displacements $\leqslant 10^{-3}$ Å). Third, O atom attracts additional electron density from next nearest neighbour (NNN) nitrogen ions and has the effective charge of −1.37 e, slightly smaller than host N ions (−1.66 e).

Using modified Eq. (1) and a 54 atom supercell containing O substitutional nearby the vacancy, we studied how O impurity affects the vacancy formation energies. Despite the fact that such O atom produces only small lattice perturbation in N site, its effective charge is smaller than that of a host N ion. As a result, the calculated formation energies for $V_{\rm N}({\rm O}) = 9.74$ eV and $V_{\rm U}({\rm O}) = 9.27$ eV, that is slightly differ from those in a host UN matrix. The $V_{\rm N}$(O) formation energy is larger whereas for $V_{\rm U}$(O) it is smaller, due to the smaller Coulombic repulsion and attraction energies between O and removed N (U) ions, respectively, as compared to the interactions in a pure UN. However, these formation energy changes are rather small and do not exceed 6%.

3.1.2. The electronic structure

Fig. 2(a) shows the projected density of states (DOS) for pure UN crystal which indicates a considerable overlap of the U 5f,6d and N 2p orbitals leading to the reduced effective charges and 5f electron delocalisation (probably, overestimated in plane-wave calcula-

Table 2
Basic properties of O substitutional impurity: incorporation (I), solution (S), and relaxation (R) energies (eV), atomic effective charges Q (in e), and local displacements Δ (in Å)

I	R	S	Q(O)	Q(N)	Q(U)	ΔN	ΔU
−9.24	0.0	−0.13	−1.37	−1.63	1.66	0.0	0.0

Table 3
The interstitial O atom in the equilibrium and saddle point positions: incorporation (I) and relaxation (R) energies (eV), atomic effective charges Q (in e), and local atomic displacements Δ (in Å)

position	I	R	Q(O)	Q(N)	Q(U)	ΔN	ΔU
Equilibrium	−5.78	2.06	−1.10	−1.49	1.76	0.277	0.065
Saddle point	−2.93		−1.24	−1.41	1.71	0.580	0.330

tions). The Bader effective charges in UN are ±1.66 e, smaller than the preliminary theoretical estimate of ±2.3 e [7].

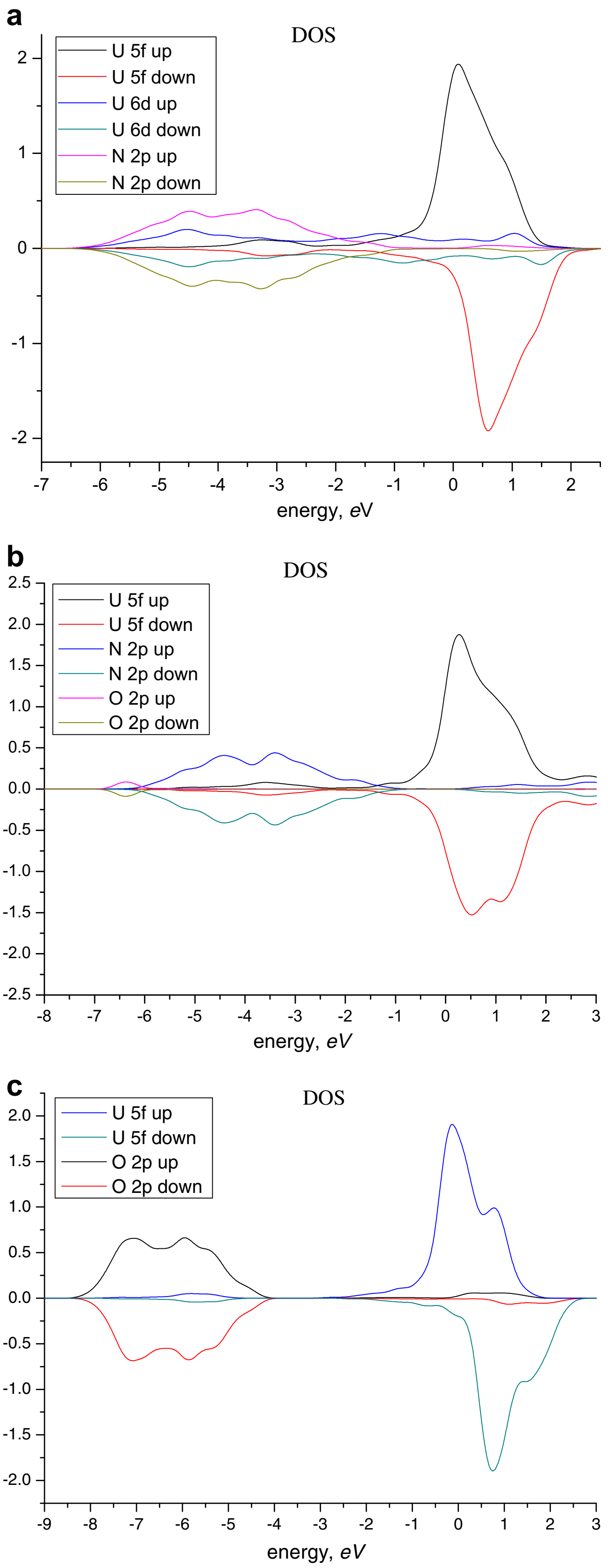

Fig. 2. The projected DOS for pure UN (a), UN with O impurity (3.7%) (b) and UO crystal (c) with the same atomic structure as UN.

The projected DOS for O impurity in UN (3.7%) is presented in Fig. 2(b). One can see that O impurity gives an additional peak at the low energy side of the N 2p DOS, around 6–7 eV below the Fermi energy. This is in agreement with the UPS experimental data observed in thin films of UO$_x$N$_{1-x}$ oxinitrides by Gouder et al. [7,8].

Lastly, the DOS for a metastable UO crystal (with the same atomic structure as UN) is plotted in Fig. 2(c). The conclusion could be drawn that the O 2p band is narrowed and shifted to the low energy side, as compared with the UN. This is in line with previous theoretical and experimental data [8,24], respectively and should lead to a stronger U 5f electron localisation.

3.2. Interstitial O impurity

3.2.1. Equilibrium position

The interstitial O atom was calculated using large 128 atom supercells. In its equilibrium position in a cube center (Fig. 2(b)) it considerably expands the surrounding lattice, which results in large displacements of four pairs of nearest ions (mostly, N) and the relaxation energy of 2 eV. It attracts considerable electronic density, thus transforming into the negatively charged ion, on expense of the four surrounding N ions. The incorporation energy is strongly negative, −5.78 eV. In this case, it coincides with the solution energy, i.e. O penetration into the interstitial position is energetically favourable.

3.2.2. Diffusion of interstitial O atoms

In the saddle point position, when the interstitial O atom passes along the (1 0 0) direction the cube side (Fig. 2(c)), its energy increases by 2.84 eV. This is in fact the *migration energy*. Simultaneously, its effective charge increases up to −1.24 e, whereas other atomic charges do not change considerably. The calculated lattice distortion of the lattice around oxygen at the saddle point (2N and 2U ions) is much larger than in the equilibrium state.

The total and difference electronic density distribution for the interstitial O atom is plotted in Fig. 3. As one can see, the O atom is strongly polarised which means that its classical modelling needs incorporation of electron shells. This atom shows large additional electron density with respect to the neutral atom, in the line with calculated effective charge of −1.1 e. The perturbation caused by the O atom is local and limited to nearest neighbours.

4. Conclusions

We have demonstrated that the atomic scale DFT-GGA (PW-91) plane-wave calculations with scalar relativistic pseudopotentials as implemented in the standard VASP code (combined with a supercell approach) can be successfully applied to model impurities in actinides, in particular, O in UN fuel. O impurities are able to penetrate easily into UN lattice and oxidize the fuel which agrees well the results of experimental studies [2,8]. The oxygen incorporation into (pre-existing) N vacancy is energetically more favourable than into the tetrahedral interstitial position [8]. However, it is energetically favourable even to create N vacancy and place O atom therein. The estimated effective oxygen charges are far from O^{2-} ion commonly used in the SM and MD simulations, the more so, the interstitial O ion is strongly polarized which needs use of the electronic shell in pair potential modelling. This is why use of the Reax Force Field approach [25] seems very promising for multi-time-scale defect simulations in nuclear fuels.

It is desirable to check the main results of these calculations using independent method (*ab initio* and/or Reax Force Field). Modelling of the UN surface oxidation and defect migration is in progress.

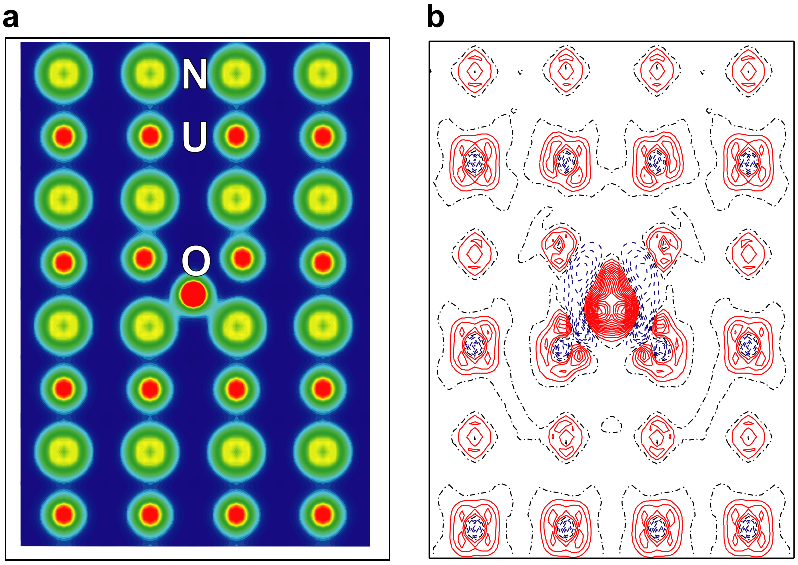

Fig. 3. The total (a) and difference (b) electron density maps for the interstitial O atom in UN lattice. The latter is the difference of the self-consistent total density for a defective crystal minus a sum of the density of a single O atom and the density of the perfect crystal. Red is an excess of the electron density, blue its deficiency.

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