# Ab initio modeling of oxygen impurities incorporated within UN (001) surface and subsurface vacancies.

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#### Motivation

Uranium mononitride is a promising nuclear fuel material for novel Generation IV reactors [1]. The oxygen impurities always present in uranium mononitride (UN) lead to its unwanted pollution and further degradation in air.

Top shed more light on importance of UN oxidation mechanism, in this study we focus on the incorporation of oxygen impurities into the N- and U- vacancies of the UN(001) surface.

### Theoretical background

For simulation of defective UN(001) substrate with empty and oxygen-occupied vacancies we employ the DFT plane wave computer code VASP 4.6 [2], using ultra-soft pseudopotentials combined with the PAW method. We use the non-local exchange-correlation functional within the Perdew-Wang-91 Generalized Gradient Approximation (PW91 GGA) [3] as well as the scalar relativistic pseudopotentials for 76 U core electrons (with  $6s^26p^66d^25f^2s^2$  valence shell) and 2 N and O core electrons (with  $2s^22p^3$  and  $2s^22p^4$  valence shells, respectively). The Monkhorst-Pack scheme [4] with a 8×8×1 *k*-point meshes in the Brillouin zone is used while the cut-off energy is set to be 520 eV.

# Surface model

For the UN(001) substrate possessing the fcc rock-salt structure, we use a slab model consisting of 5, 7 or 9 atomic layers. The 2D slabs are separated by a vacuum gap of sixteen interlayer distances (38.88 Å) (Fig 1).

We use the supercells with 2×2 and 3×3 extensions of translation vector for the (001) surface of UN (Fig. 2). Due to a presence of mirror plane in the symmetric slabs, one can consider the two-sided symmetric arrangement of defects.

The lattice constant of UN slabs is fixed at 4.87 Å, taken from the lattice relaxation of UN bulk [5]. In taken from the lattice relaxation of UN bulk [5]. In all the calculations, we perform the structural optimization within the supercell of fixed linear dimensions. The total spin magnetic moment is also relaxed in all the calculations for the ferromagnetic spin arrangements on the uranium sub-lattice.



Fig. 1: Cross-

section of 3D UN

Vacuum gap (16 interplane distances)

UN slab (4, 6, or 8 interplane distances)

· N·O

Fig. 2: The symmetrical 5-layer UN(001) slab with a 2×2 (left) and 3×3 (right) periodicity of the oxygen atoms incorporated into the surface N-vacancies

### Electron density re-distributions

Inside the 5-layer slab, a presence of the two symmetrically positioned defects induces their visible interaction (charge re-distribution across a slab, Fig. 3a). By increasing the slab thickness one can reduce this effect (Fig. 3b). If the supercell size is decreased (the 2×2 extension, Fig. 3c) an additional electron density parallel to the surface plane is observed between the defects. Similar effects are also observed for re-distributions of the electron density around defects in the mirror planes (Fig. 4).



Fig. 3: The 2D sections of the electron charge density re-distributions  $\Delta \rho(\mathbf{r})$  around the O atoms



incorporated into the surface Nvacancies of the five- and sevenlaver UN(001) slabs with 2×2 and supercell extensions.  $\Delta \rho(\mathbf{r})$  are defined as the total electron density of the O-containing defected surface minus a superposition of the electron densities of the surface containing the N-vacancies and the O atom in the regular positions on the surface. Solid (red) and dashed (blue) isolines correspond to positive and negative electron density, respectively.

Fig. 4: The 2D sections of  $\Delta \rho(\mathbf{r})$ around the O atoms incorporated into the N-vacancies disposed in central laver of the seven-laver UN(001) slabs with 2×2 and 3×3 supercell extensions

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### Incorporation and solution energies

The energy balance for the incorporation of O atom into a vacancy can be characterized by the incorporation energy I:  $I = E_{O_{-inc}}^{N(U)} - E_{Vac}^{N(U)} - E_{O}$   $I = \frac{1}{2}(E_{O_{-inc}}^{N(U)} - E_{Vac}^{N(U)} - 2E_{O})$  for surface or sub-surface layer.

Here  $E_{\Omega \ inc}^{N(U)}$  is the total (negative) energy of the supercell containing the O atom at either the N- or U-vacancy,  $E_{\rm vocm}^{\rm NO}$  is the energy of the supercell containing an unoccupied (empty) vacancy, and  $E_{\rm o}$  a half of the total energy of isolated O<sub>2</sub> molecule in the triplet state.

Since the value of *I* describes the energy balance for the incorporation into pre-existing vacancies, it has to be negative for energetically favorable incorporation processes.

To take into account the total energy balance, including the vacancy formation energy in the defectless slab, we

define the solution energy:  $S = I + E_{form}$ Here  $E_{form}$  is the formation energy of N- or U- vacancy in the slab (Defective UN surface containing both nitrogen and uranium vacancies disposed at different positions within the UN (001) slab has been also discussed in a separate paper [6]).

Table 1: Incorporation (I) and solution (S) energies in eV and average spin magnetic moments of U atoms in  $\mu_B$  for O incorporation into the UN(001) surface. The reference states for calculating the incorporation and solution energies are the chemical potentials of O, N and U calculated for O<sub>2</sub>, N<sub>2</sub> molecules and  $\alpha$ -U, respectively

The O incorporation into the N-vacancies energetically favorable since the calculated values of *I* and S are strictly negative (Table 1). That is, it is energetically favourable to create the N-vacancy and adsorb the O atom from air. Table 1 also from air. Table 1 also indicates that solution of atoms is more oxygen the energetically favorable at the surface planes of the UN surface.

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	Supersell size	Number of atomic layers in slab	N vacancy			U vacancy		
			I	\$	$\mu_{av}^{U}$	1	S	$\mu_{\scriptscriptstyle ov}^{\scriptscriptstyle U}$
Surface layer	2x2	5	-6,173	-2.473	1.65	-0.339	1.120	1,16
		7	-6.181	-2.476	1.49	-0.855	0.583	1.36
		9	-6.188	-2.479	1.41	-0.943	0.493	1.31
	3x3	5	-6.122	-2.481	1.60	-0.683	0.654	1.48
		7	-6.126	-2.480	1.46	-1.073	0.230	1.38
Subsurface layer	2x2	5	-6.314	-2.068	1.64	-1.856	1.284	1.66
		7	-6.419	-2.090	1.49	-1.823	1.297	1.45
		9	-6.417	-2.091	1.41	-1.823	1.271	1.38
	3x3	7	-6.428	-2.093	1.46	-2.012	1.000	1.43
Central (mirror) layer	2x2	7	-6.611	-2.180	1.47	0.736	3.923	1.44
		9	-6.608	-2.192	1.39	0.669	3.838	1,38
	3x3	7	-6.599	-2.182	1.45	0.317	3.378	1.47

Density of states

In Fig. 5 the total and projected density of states (DOS) is shown for the 7-layer defective UN(001) substrate with the O atom incorporated into the N-vacancy. The system remains conducting throughout all the calculations with the significant contribution from the U 5f states at the Fermi level similar to pure UN bulk [5]. The appearance of the specific O 2p band with an energy peak at -6 eV is observed

When comparing the DOSs constructed for the O atoms incorporated into the N-vacancies, a noticeable shift of the O 2p band (by about -1.0 eV) distinguishes the surface plane from the internal lavers. Moreover, in the case of the surface plane, this band Internal layers. Moreover, in the case of the surface plane, this band well overlaps with the N 2p band, partly mixed with the U 5f states (similar effects happen with the O<sub>2</sub> molecule atop the surface U atom [7]). Contrary, the O 2p band is quasi-isolated from the other bands (analogously to the O atom incorporated into the N-vacancy in UN bulk [8]). Note that position of the N 2p band is insensitive to the presence of O atoms and lies within -6 and -1 eV.

### Spin magnetic moments

Analogously to defective UN substrate with empty vacancies and pure slab averaged spin density of uranium atoms decreases with a number of layers in the slab for both types of the vacancies (except for the O atom incorporated into the U-vacancy in the surface plane) (See Table 1)

Fig. 5: The total and projected DOS for three positions of O

atoms incorporated at N vacancies with a 3×3 periodicity across the 7-layer UN(001) slab: a) surface layer, b) sub-surface layer, c) central layer. The highest peaks have been normalized to the same value, whereas a convolution of individual energy levels has been plotted using the Gaussian functions with a half-width of 0.2 eV.

### Conclusion

Performed calculations allow us to predict the following stages for reactivity of oxygen positioned atop the UN(001) surface:

(i) to break the O2 chemical bond [7], (ii) to locate the newly-formed O adatoms atop the surface U atoms [9]

(iii) to incorporate adatoms in existing surface N vacancies as a result of surface diffusion.

(iv) to incorporate oxygen atoms in existing subsurface N vacancies as a result of inter-lattice diffusion.

This explains an easy UN oxidation observed in air. Moreover, we predict a formation of oxynitrides near the UN(001) surface with a partial involvement of U-vacancies in oxidation process too.

We have analyzed relevant effects of the electronic charge re-distribution which demonstrates a quite local nature We have analyzed relevant energies on the electronic charge recursional which demonstrates a quie local nation of the density perturbation caused by inserted O atoms. The analysis of density of states shows both overlapping of the O 2p states with the N 2p states at initial stages of oxidation (*surface incorporation*) and separation of the O 2p states from other bands in the case of deeper penetration of oxygen atoms (*subsurface penetration*). The results of this analysis could be used for the experimental UPS identification and comparison.

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