

A comparative study of the UN(100) and (110) surfaces: first principles DFT calculations

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Motivation

The uranium mononitride (UN), which possesses a rock-salt (NaCl) structure and metallic nature, is an advanced material for the non-oxide nuclear fuel considered as a promising candidate to be used in Generation-IV nuclear reactors. However, UN samples synthesized for reactors contain considerable amount of O impurities, which greatly affect fuel properties. Therefore, it is necessary to understand the mechanism of both oxygen adsorption and further oxidation of uranium mononitride. Synthesized specimens of polycrystalline UN contains particles with differently oriented crystallographic facets [1]. To simplify modeling of the oxygen interaction with UN surface, we study mainly the (001) surface since according to Tasker analysis [2] it has the lowest surface energy. Nevertheless, real UN particles contain facets with different crystallographic orientation. To increase validity of our results, we have additionally performed (110) surface calculations. We chose (110) surface orientation for additional calculations since alternative low-indexed (111) surface contains charged planes and its calculation requires artificial approaches. Moreover, strong reconstruction must occur, in order to stabilize polar (111) surface. Less densely-packed UN(110) surface is characterized by smaller interlayer distance in z direction as compared to (001) surface (Table 1 and Fig. 1). We simulated reconstruction of perfect and defective UN(110) surface as well as atomic oxygen adsorption, formation of N vacancies and oxygen incorporation into them.

| | (001) surface | (110) surface |
|---|--|---|
| Size of surface unit cell (ÅxÅ) | 3.44 × 3.44 ($\frac{\sqrt{2}}{2}a \times \frac{\sqrt{2}}{2}a$) or ($\frac{1}{2}a \times a$) | 4.87 × 3.44 ($a \times \frac{\sqrt{2}}{2}a$) |
| Distance between two nearest U and U (or N and N) atoms in xy plane (Å) | 3.44 ($\frac{\sqrt{2}}{2}a$) in both directions | 4.87 in x direction 3.44 in y direction |
| Distance between nearest U and N atoms in xy plane (Å) | 2.435 ($\frac{a}{2}$) | 2.435 ($\frac{a}{2}$) in x direction not defined in y direction |
| Distance between neighbor layers in z direction (Å) | 2.435 ($\frac{a}{2}$) | 1.72 ($\frac{a\sqrt{2}}{4}$) |
| Distance between nearest atoms in z direction (Å) | 2.435 ($\frac{a}{2}$), distance between U and N atoms | 3.44 ($\frac{\sqrt{2}}{2}a$), distance between N and N (or U and U) atoms |

Table 1. Comparison between the UN(001) and UN(110) surfaces (a is a lattice constant of cubic fcc crystal).

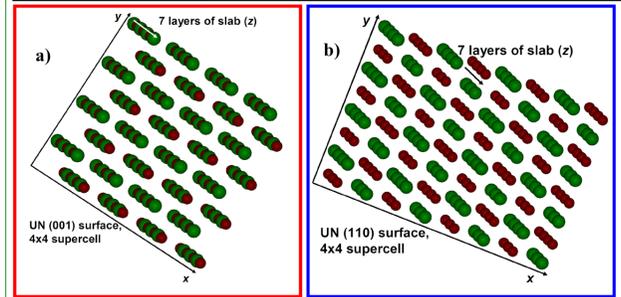


Fig. 1. Structural comparison of slabs used for simulation of (001) (a) and (110) (b) UN surfaces.

Computational method and model

For simulation of pure and defective UN(001) and (110) substrates with empty and oxygen-occupied vacancies, we employ the DFT plane-wave computational package VASP 4.6 [3], using ultra-soft pseudopotentials combined with the PAW method. We use the Perdew-Wang-91 GGA non-local exchange-correlation functional [3] and the scalar relativistic PAW pseudopotentials representing the core electrons of U (with $6s^2 6p^6 6d^5 7s^2$ valence shell), N ($2s^2 2p^3$) and O ($2s^2 2p^4$) atoms (containing 14, 5 and 6 valence electrons, respectively). The cut-off energy is chosen to be 520 eV. We use the Monkhorst-Pack scheme [4] for 4x4x1 and 8x8x1 k-point meshes in the Brillouin zone (BZ).

For the UN(001) and (110) substrates, we use 3D slab model consisting of 5-11 atomic layers with primitive cell as well as 2x2 and 3x3 supercells (Fig. 3). The 2D atomic slabs are separated by a vacuum gaps of ~40 Å (Fig. 2).

The lattice constant of UN slabs is fixed at 4.87 Å, 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 on the ferromagnetic spin distributions within the uranium sub-lattice.

Fig. 2. Cross-section of 3D UN slabs.

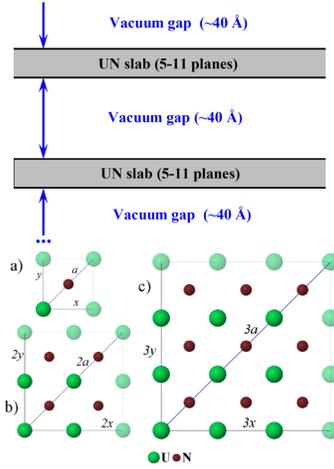


Fig. 3. Atop views of primitive cell (a) as well as 2x2 (b) and 3x3 (c) supercells upon UN(001) surface.

Table 4. Nitrogen vacancy formation energies (in eV) as well as averaged magnetic moment μ_{av} of U atom evaluated for UN(001) and (110) surfaces.

| Number of layers and supercell size | N vacancy E_{form} on (001) surface | $\mu_{av}(\mu_B)$ (001) | N vacancy E_{form} on (110) surface | $\mu_{av}(\mu_B)$ (110) |
|-------------------------------------|---------------------------------------|-------------------------|---------------------------------------|-------------------------|
| 5, 2x2 | 3.700 | 1.702 | 3.075 | 1.818 |
| 7, 2x2 | 3.706 | 1.548 | 3.028 | 1.585 |
| 9, 2x2 | 3.708 | 1.452 | 3.036 | 1.512 |
| 11, 2x2 | 3.712 | 1.392 | 3.026 | 1.453 |
| 7, 3x3 | 3.646 | 1.487 | 2.966 | 1.498 |

$$E_{form}^{N(U)vac} = \frac{1}{2}(E^{UN(N,vac)} + 2E^N - E^{UN})$$

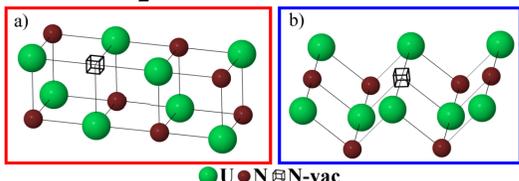


Fig. 5. 2-layer models of N vacancy on UN(001) (a) and (110) (b) surface

To increase the reliability of the results we also compare the results of calculations on N vacancies in surface layer upon UN(001) [6] with analogous calculations on (110) surface (Fig. 5). All basic tendencies remain similar for vacancies on (110) surface. Averaged magnetic moment μ_{av} decreases as a function of a number of layers in the slab for both surfaces. On the other hand, vacancy formation energies are by ~0.7 eV smaller for UN(110) surface. This distinction is easy explainable due to a larger friability of the (110) surface as compared to the (001) surface.

Table 5. The calculated binding energies (E_{bind} , eV) for oxygen adsorption atop UN(001) and (110) surfaces.

| Number of layers and supercell size | Atop U | | Atop N | |
|-------------------------------------|--------------------|------|--------------------|--|
| | Binding energy, eV | | Binding energy, eV | |
| (001) | 7, 2x2 | 7.51 | 5.58 | |
| | 7, 3x3 | 7.57 | 5.65 | |
| (110) | 7, 2x2 | 7.90 | 5.73 | |
| | 7, 3x3 | 7.91 | 5.99 | |

$$E_{bind} = \frac{1}{2}(E^{UN} + 2E^{O_{triple}} - E^{O/UN})$$

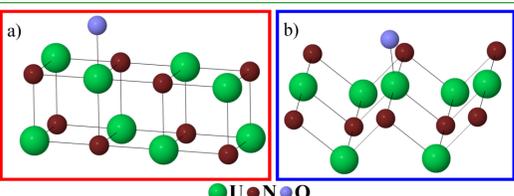


Fig. 6. 2-layer models of oxygen adsorption atop surface U atom on UN(001) (a) and (110) (b) surface

We have also estimated the binding energies of oxygen adatom with UN(110) surface (Table 5). We have found these results qualitatively similar to those for O adsorption on (001) surface. For both surfaces, oxygen binding energy with U atom is larger as compared to that with N atom (~1.9 eV for (001) and ~2.1-2.2 eV for (110) surface). Moreover, increase of the surface supercell from 2x2 to 3x3 leads to slight growth of binding energy. Oxygen binding energies on (110) surface are ~0.1-0.4 eV larger as compared to (001) surface. Higher E_{bind} values for (110) surface can be explained by larger distances between surface adatoms upon (110) surface resulting in decreased interactions between adsorbed oxygen and all other atoms, excluding underlying U or N atom.

$$E_I = \frac{1}{2}(E^{UN(O-inc)} - E^{UN(N,vac)} - 2E^O)$$

$$E_S = E_I + E_{form}$$

Fig. 7. 2-layer models of oxygen incorporation into surface N vacancy on UN(001) (a) and (110) (b) surface

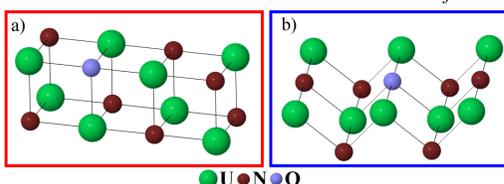


Table 6. Incorporation (E_I) and solution (E_S) energies, average spin magnetic moments of U atoms and effective charge on O atoms for oxygen incorporated into N vacancy on UN(001) [7] and (110) surfaces. The reference states for calculations on the incorporation and solution energies are the chemical potentials of O and N calculated for O₂ and N₂ molecules, respectively (2x2 and 3x3 supercells).

| Number of layers | (001) surface | | | | (110) surface | | | |
|------------------|---------------|------------|--------------------------|-----------------------------|---------------|------------|--------------------------|-----------------------------|
| | E_I (eV) | E_S (eV) | μ_{av}^U (μ_B) | q_{eff} (e ⁻) | E_I (eV) | E_S (eV) | μ_{av}^U (μ_B) | q_{eff} (e ⁻) |
| 5, 2x2 | -6.173 | -2.473 | 1.647 | -1.36 | -5.853 | -2.778 | 1.736 | -1.27 |
| 7, 2x2 | -6.181 | -2.476 | 1.495 | -1.36 | -5.822 | -2.794 | 1.516 | -1.29 |
| 9, 2x2 | -6.186 | -2.479 | 1.412 | -1.36 | -5.820 | -2.784 | 1.472 | -1.29 |
| 11, 2x2 | -6.195 | -2.483 | 1.365 | -1.35 | -5.817 | -2.791 | 1.416 | -1.29 |
| 7, 3x3 | -6.126 | -2.480 | 1.463 | -1.36 | -5.748 | -2.783 | 1.471 | -1.28 |

It could be interesting further to compare incorporation (E_I) and solution (E_S) energies for two surfaces. Table 6 compares these energies as function of slab thickness and supercell size. One can see that the UN(110) surface is characterized by more negative solution energy, even though the difference between their solution energies is ~0.3 eV. On the other hand, the incorporation energy changes this trend suggesting more negative values for the (001) surface. Moreover, the difference between incorporation energies approaches to 0.4 eV. Such results demonstrate importance of E_I calculations as our surface might function under extreme conditions like high temperatures (Table 6).

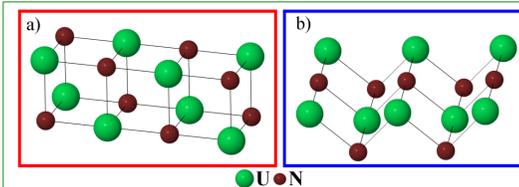


Fig. 4. 2-layer models of UN(001) (a) and UN(110) (b) surfaces.

$$E_{surf}(n) = \frac{1}{2S}(E_n - nE_b)$$

Table 2. Surface energies E_{surf} (J·m⁻²) and averaged magnetic moments (in μ_B) of U atom for the defectless UN(001) [5, 6] and UN(110) surfaces. In spin-frozen calculations, μ was chosen to be 1 μ_B .

| Number of layers | E_{surf} (J·m ⁻²) | | μ_{av} (μ_B) | |
|------------------|---------------------------------|-------------------------|------------------------|-------|
| | spin-frozen slab (001) | spin-relaxed slab (001) | (001) | (110) |
| 5 | 1.69 | 1.44 | 1.57 | 1.645 |
| 7 | 1.70 | 1.37 | 1.44 | 1.464 |
| 9 | 1.70 | 1.29 | 1.37 | 1.417 |
| 11 | 1.69 | 1.22 | 1.33 | 1.385 |

| Atom | Number of UN(001) slab atomic layers | | | Number of UN(110) slab atomic layers | | |
|-----------------------------|--------------------------------------|-------|-------|--------------------------------------|-------|-------|
| | 5 | 7 | 9 | 5 | 7 | 9 |
| Surface U | 1.68 | 1.74 | 1.68 | 1.46 | 1.48 | 1.48 |
| Sub-surface U | 1.67 | 1.63 | 1.63 | 1.67 | 1.88 | 1.83 |
| U in central (mirror) plane | 1.69 | 1.72 | 1.65 | 1.66 | 1.60 | 1.74 |
| Surface N | -1.65 | -1.67 | -1.67 | -1.68 | -1.55 | -1.55 |
| Sub-surface N | -1.68 | -1.70 | -1.70 | -1.67 | -1.75 | -1.73 |
| N in central (mirror) plane | -1.74 | -1.65 | -1.65 | -1.63 | -1.70 | -1.71 |

Table 3. Atomic Bader charges for the defectless spin-relaxed UN(001) and (110) surfaces.

The calculations of the effective atomic charges q_{eff} , average magnetic moments μ_{av} of U atoms, and surface energies E_{surf} for defect-free slabs of different thicknesses (Tables 2 and 3) have been performed, in order to check how these properties depend on atomic spin relaxation. The spin relaxation leads to considerable change of the E_{surf} depending on the number of layers in a slab (Table 2). The largest μ_{av} value was obtained for U atoms in the 5-layer slab, i.e., μ_{av} slightly decreases with the thickness suggesting difference of 0.3 μ_B between the 5- and 11-layer slabs. The lattice relaxation energies in spin-relaxed calculations turn out to be quite small, i.e., ~0.03 eV.

Depending on slab thickness, the surface energies are ~0.5-0.7 J·m⁻² larger for UN(110) surface (Table 2). It means that the UN(001) surface is energetically more favorable.

It is also interesting to analyze q_{eff} values for atoms across the slab as a function of the number of layers in a slab (Table 3). First, these q_{eff} show considerable covalent bonding both on the surface (e.g., sub-surface) and on the central plane since the values. Second, due to different reconstruction mechanisms of UN(001) and UN(110) surfaces, the atomic charges are different too: ionicity of bonds at (001) surface is higher, thus leading to certain difference in surface properties.

Summary

1. Depending on slab thickness, the surface energies are ~0.5-0.7 J·m⁻² larger for UN(110) surface (Table 1). It means that the UN(001) surface is energetically more favorable.
2. Energies of the nitrogen vacancy formation on the uranium mononitride surface are larger for (001) surfaces, by ~0.7 eV irrespectively of slab thickness.
3. Ionicity of bonds at (001) surface is higher, thus leading to certain difference in surface properties.
4. Oxygen binding energies on (110) surface are ~0.1-0.4 eV larger as compared to (001) surface. Nevertheless, we clearly see similar tendencies for both surfaces.

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References

- [1] G.W. Chinthaka Silva, Ch.B. Yeaman, L. Ma, G.S. Cerefice, K.R. Czerwinski, and A.P. Sattelberger, *Chem. Mat.*, 20 (2008) 3076.
- [2] P.W. Tasker, *J. Phys. C: Solid State Phys.*, 12 (1979) 4977.
- [3] G. Kresse and J. Hafner, *VASP the Guide* (University of Vienna, 2007).
- [4] J.P. Perdew and V. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [5] R.A. Evarestov, A.Y. Bandura, M.V. Losev, E.A. Kotomin, Yu.F. Zhukovskii, and D. Bocharov, *J. Comput. Chem.* 29 (2008) 2079.
- [6] D. Bocharov, D. Gryaznov, Yu.F. Zhukovskii, E.A. Kotomin, *Surf. Sci.*, 605 (2011) 396.
- [7] D. Bocharov, D. Gryaznov, Yu.F. Zhukovskii, E.A. Kotomin, *J. Nucl. Mater.*, 416 (2011) 200.