JOURNAL OF NANO- AND ELECTRONIC PHYSICS *ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Vol. **7** No 4, 04018(5pp) (2015) Том **7** № 4, 04018(5cc) (2015)

First Principle Study of Uranium Nitrides UN and UN_2 Using DFT and DFT + U

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(Received 03 September 2015; published online 10 December 2015)

First principle calculation based on density functional theory (DFT) was used to evaluate some physical properties of Uranium Nitrides. Adsorption of oxygen O atom and O_2 molecule on/in (001) surfaces of both Uranium monoNitride (UN) and diNitride (UN_2) was then studied and compared mutually. To treat the strong correlation effects caused by 5f Uranium valence electrons, Hubbard-U advanced (DFT + U) approach was employed to correct the exchange correlation functional GGA and PBE which are based on generalized gradient approximation. The functional are developed for the Vienna Abinitio Simulation Package (VASP) and were used with the projector-augmented wave (PAW) pseudo potentials.

The structural and elastic-mechanical UN and UN_2 properties were calculated within DFT and DFT + U methods. Then, Potential Energy Surfaces (PES) concepts which correspond to the interaction between O atom (respectively O_2 molecule) and (001) on-surfaces / sub-surfaces uranium nitrides for several positions were determined to identify favorable adsorption sites.

Physical properties calculation results of UN or UN_2 are in order of magnitude of other theoretical values and show an acceptable precision compared to experiments. Hubbard U value of the DFT + U formalism was optimized to achieve Antiferromagnetic (AFM) UN configuration and was effective at $U = 1.625$ eV. Optimization of UN_2 was accomplished to attain experimental cell parameter of 5.31 A° and was reached for $U = 2.6$ eV.

According to our calculation results, O_2 diffusion through UN(001) and UN_2(001) clean surfaces have demonstrated dissociation of the molecule from a distance of approximately $d = 1.5$ Å. Favored on surface modes for O atom adsorption were found to be near the bridge site for UN(001) and UN_2(001). The O incorporation through UN(001) surface was at the bridge site, nevertheless, for UN_2, merging of O atom in the (001) surface bridge site was not allowed.

Keywords: First principle, DFT, DFT+U, Hubbard U, Uranium Nitride, UN, UN_2, PES, Atom relaxation.

PACS numbers: 63.20.dk, 77.84.Bw

1. INTRODUCTION

Uranium nitrides are considered as promising fuel materials for the generation-IV fast breeder reactors, because of some physical properties advantages compared to oxides fuel. The high metal density and the better thermal properties at high temperatures of uranium nitrides are of the main reasons but also they show some other physical behaviors qualities like good phase stability and high melting point [1].

Density Functional Theory (DFT) have demonstrated agreement results compared to experiments for a number of uranium nitrides physical properties, but, for other properties, some differences from experimental values are noticeable example of the anti-ferromagnetic (AFM) configuration of UN which cannot be reproduced by standard DFT calculations. The f electrons configuration partially filled of the uranium atom causes a strong coulomb correlation and then unreasonable ground states distorted the real equilibrium state of materials [2].

Among solutions, DFT + U formalism developed by Dudarev et al [3] which consists of adding a depending functional on the parameter U (Hubbard value) to the conventional one to force the on-site Coulomb repulsion is a method which allow the correction of the DFT calculations of strongly correlated materials like uranium nitrides or oxides and most of actinides [4, 5, 6].

In this work, we report on a comparative study of some physical properties of uranium mononitride (UN) and uranium dinitride (UN_2), adsorption study of oxygen (atom and molecule) through (001) surfaces (UN and UN_2) are then performed to identify the uranium nitride favorable site which present the maximum oxygen adsorption energy.

Consequently, lattice parameter, elastic and mechanical properties of Uranium nitrides UN and UN_2 were calculated within the conventional exchange functional and the Hubbard-U approach for several values of U. To find the Hubbard optimum value $U = U_{optim}$, where the optimizing study was performed according the experimental physical properties of UN (magnetic configuration) and UN_2 (cell parameter).

2. METHODOLOGY AND COMPUTATIONAL

All the calculations were performed using VASP (Vienna Abinitio Simulation Package) version 5.3. The code is based on the plane-wave method using density functional theory (DFT) to determine total energies [7, 8, 9].

We have used two Gradient Generalized Approximation functional available in the VASP package, the GGA-91 [10] and the Perdew-Burke-Ernzrhof (PBE.52) [11] with the projector-augmented wave (PAW) pseudo potentials [12], in which the Uranium $6s^2 6p^6 6d^2 5f^2 7s^2$ and nitrogen $2s^2 2p^3$ electrons were considered as valence electrons.

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To evaluate correctly electronic structure of materials owning strong Coulomb correlations caused by the Uranium 5*f* electrons, the covariant version of the DFT+U energy functional proposed by Dudarev et al was applied.

$$E_{DFT+U} = E_{DFT} + \frac{1}{2}(U-J)\sum_{\sigma}\left\{T_r\rho^{\sigma} - T_r\left(\rho^{\sigma}\right)^2\right\}$$

Where ρ represents the density matrix of *f* electrons, σ is the projection of spin, *U* and *J* are the spherically averaged matrix elements of screened Coulomb electron-electron interaction. As the above equation shows, the total energy depends on the parameters *U* and *J*, where the difference $U = (U - J)$ is meaningful.

Parameter *J* for Uranium atom is taken equal to 0.51 eV as Dorado et al [13] have determined. Parameter $U = U - J$ is a variable in our study.

Preliminary DFT calculations permit to calculate cutoff energy which ensures sufficient plane waves for the electron wave functions and k-point grid in the Brillouin zone developed by Monkhorst & Pack mesh method [14]. For the two uranium nitrides (UN and UN_2) from a 400 eV cutoff energy and (7 × 7 × 7) mesh *k*-point grid let total energies converge and assure precisions less than 10^{-4} eV per atom.

Mechanical properties such as Bulk modulus, Poisson ratio, stiffness and stability of materials [15, 16] are deducted from elasticity study via Voigt-Reuss-Hill relations [17]. In addition, Bulk modulus is derived from another method based on the fitting of the energy-volume data and using the third-order Birch-Murnaghan equation of states (EOS) [18].

For adsorption comparison study, UN surface is modeled by a five-layers and the UN_2 surface is represented by a five layers slab terminated U or a six layers slab terminated N, separated both by a sufficient 20 Å of vacuum space. Oxygen is placed on one side of the slab where the induced dipole moment is taken into account by applying a dipole correction [19].

The adsorption energy ($E_{adsorption}$) is considered as a measure of the strength of adsorbate-substrate adsorption. It is defined as [20, 21]:

$$E_{(ad\_O)} = -1/N_O[E_{(O/UN)} - (E_{UN} + N_O E_O)].$$

Where E_{ad_O} is the average adsorption energy per oxygen atom on the surface, N_O is the number of oxygen atoms in the surface unit cell, $E_{O/UN}$, E_{UN}, and E_O represent the total energy of the adsorbate-substrate system, the clean surface, and the free oxygen atom, respectively. So, positive number indicates that the adsorption is exothermic (stable) and a negative number indicates an endothermic process.

3. RESULTS AND DISCUSSION

3.1 Bulk Calculations

UN belongs to the space group fm-3m (No. 225), it's crystalline structure follows the NaCl-type ionic structure which the conventional cell is an FCC structure with four atoms of Uranium and four atoms of Nitrogen occupying all the octahedral sites.

$$U\left\{(0,0,0),\left(\frac{1}{2},\frac{1}{2},0\right),\left(0,\frac{1}{2},\frac{1}{2}\right),\left(\frac{1}{2},0,\frac{1}{2}\right)\right\};$$

$$N\left\{\left(\frac{1}{2},0,0\right)\left(0,\frac{1}{2},0\right),\left(0,0,\frac{1}{2}\right),\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)\right\}$$

UN_2 belongs to the space group fm-3m (No. 225), it's crystalline structure follows the CaF_2-type ionic structure which the conventional cell is an FCC structure with four atoms of Uranium and eight atoms of Nitrogen occupying all the tetrahedral sites. The bulk calculation was done by considering the unit cell with three atoms, one uranium at (0, 0, 0) and two Nitrogen at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) [22].

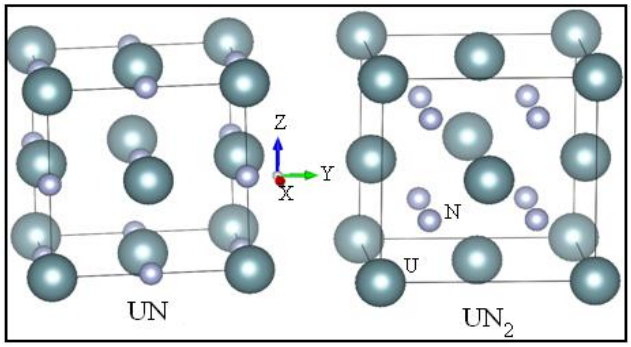

Fig. 1 – Crystalline Structure of UN and UN_2

From our calculations and using the PBE functional and PBE + U formalism, the ground state of UN shows that UN is a FM metal up to a Hubbard value of $U = U_{AFM} = 1.625$ eV and then the AFM nature takes the above. Experimental results denote an AFM configuration of UN at low temperature [23, 24].

Since UN_2 is a non magnetic (NM) material within DFT calculation [25] total energies vs Hubbard U value are insensitive to magnetic configuration.

Bulk calculations of UN were performed using DFT and DFT + U methods (PBE and GGA) the results are showed on Table 1.

Table 1 – UN structural properties using PBE+U method

Magnetic Configuration	Cell parameter (Å)	Bulk Modulus (GPa)
FM(U = 0;PBE)	4.86	198.6
FM(U = 0;GGA)	4.869	201.9
NM(U = 1.625eV ;PBE)	4.865	222.0
FM(U = 1.625eV ;PBE)	4.904	168.5
AFM(U = 1.625eV ;PBE)	4.911	199.0
Experimental [26]	4.886	194
Other theoretical [27-29]	4.83,4.952	206, 182

Results are reported for the three magnetic configurations and compared to experimental values mutually, one can see that for the cell parameter, The FM calculation gives the best precision of 0.37 % (AFM: 0.5 %) but for the bulk modulus AFM result shows better approach to experiments and the precision is about 2.5 % (FM: 13.4 %). NM configuration study of UN vs Hubbard *U* shows good results of cell parameter but a large bulk modulus compared to experimental values as mentioned in table for $U = 1.625$ eV.

Table 2 – UN_2 structural properties using DFT + U method

	Cell parameter (Å)	Bulk Modulus
DFT	5.276	252
DFT + (U = 2.6 eV)	5.31	251
Experimental [30]	5.31	No values
Other theoretical [25, 29]	5.284, 5.259	235 to 264

Table 2 summarizes some UN_2 properties calculated for the optimized Hubbard U value; $U = U_{UN2\text{-}Optim} = 2.6$ eV value which permit to achieve experimental UN_2 cell parameter. We remark that the bulk modulus didn't vary significantly with $U_{UN2\text{-}Optim}$.

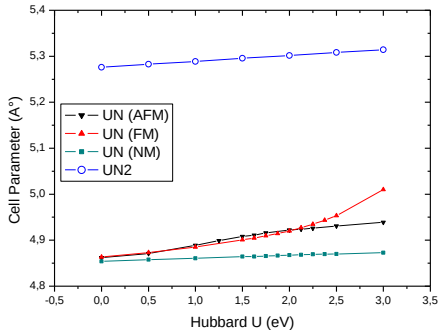

Fig. 2 – UN, UN_2, Cell Parameter vs Hubbard-U parameter

Figure 2 summarizes the progress of the variation of the UN and UN_2 cell parameter versus Hubbard U values. For UN, we noticed that the AFM configuration is the best profile response than NM or FM states; in fact AFM cell parameter values are practically close to the experimental value for Hubbard U varying from 0 to 3 eV but for FM configuration, cell parameter out of values are noticed from a Hubbard value of about $U = 2.5$ eV.

For UN_2, which is a NM material within DFT calculation total energies vs Hubbard U value are insensitive to magnetic configuration [25]. We remark that UN_2 cell parameter (a) grows slightly with the Hubbard U values; for $U = 0.5$ eV, $a = 5.28$ Å and for $U = 3$ eV, $a = 5.315$ Å.

3.2 Mechanical (Elastic) Results

UN elastic-mechanical calculations considering DFT + U approach were calculated for two magnetic configuration FM and AFM, taking the Hubbard optimization value $U = 1.625$ eV and using the approach formulas developed by Voight-Reuss-Hill for a cubic structure. For the FM state, elastic and mechanical results are deviated from the experimental ones except for bulk modulus and cell parameter which are improved (see Table 3). However for the AFM state calculations have induced non stability criteria elastic stability ($C11 < C12$) and then results are not agree with cubic system calculation [31].

Instead, UN_2 results as mentioned in Table 4 are in order of magnitude of other theoretical values [32].

3.3 Oxygen Molecule Dissociation

The dissociation of O_2 molecule approaching UN(001) surface was mentioned in the reference [36]; we have performed PES calculation for O_2 molecule which is vertical to UN(001) surface at the bridge site as illustrated in figure 3 [37].

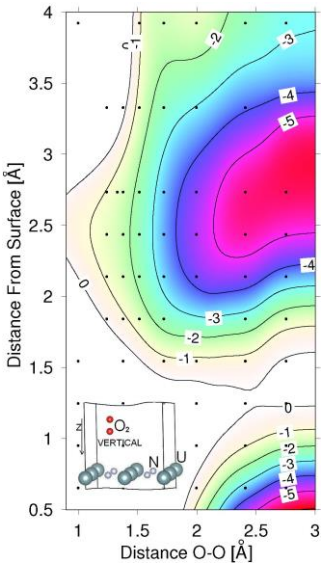

Fig. 3 – UN dissociation of O_2 molecule at vertical position in relation to UN(001) surface at the bridge site

Table 3 – UN elastic properties using DFT + U method

Magnetic Configuration	a (Å)	B (GPa)	G (GPa)	E (GPa)	ν	A
DFT-FM	4.86	219.3	75.5	203.1	0.345	0.34
FM (DFT + U = 1.625 eV)	4.90	199.8	43.3	121.2	0.39	0.047
Experimental [33, 34]	4.886	206, 184	104	267, 262, 201	0.28, 0.26	–
Other theoretical [35]	4.83	202	79.0	210	0.33	0.41

Table 4 – UN_2 elastic properties using DFT + U method

	B (EOS)	B (GPa)	G (GPa)	E (GPa)	ν	A
Our result $U_{UN2\text{-}optim} = 0$ eV	251.9	253.6	97.0	258.0	0.33	0.344
Our result $U_{UN2\text{-}optim} = 2.6$ eV	252.5	254.0	84.5	228.1	0.350	0.285
Theoretical result ($U = 2$ eV) [25]	253.5	256.4	89.4	240.2	0.344	0.318

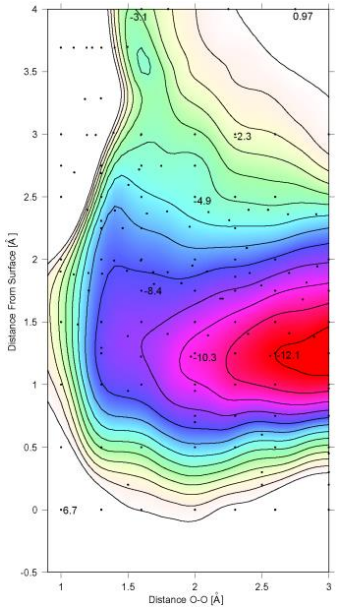

Fig. 4 – PES molecule O_2 through (001) surface Hollow site

The principle of calculation consists of a DFT energies evaluation for different positions of the molecule along the *z* axis with different distances between the O atoms composing the molecule.

The figure 3 shows that for a vertical O_2 molecule the dissociation begin far from the surface at around 2.5 Å from UN(001) surface. We remarks also, that when atoms are approaching the surface the dissociation with adsorption of atoms probability increase.

Figure 4 show that O_2 molecule is dissociated when approaching the UN_2(001) surface practically at a distance of around 1.5 Å. The oxygen molecule was horizontal to the UN_2 surface and positioned at the hollow site.

3.4 Atomic Oxygen Adsorption

Static atomic PES calculations were performed along multitude site positions on UN(001) surface (hollow, bridge Top,…) to map all adsorption energies and to deduct the more favorable one. It was found that the bridge site U-U is the preferred site for atomic adsorption on / in UN(001) surface as illustrated in the figure 5.

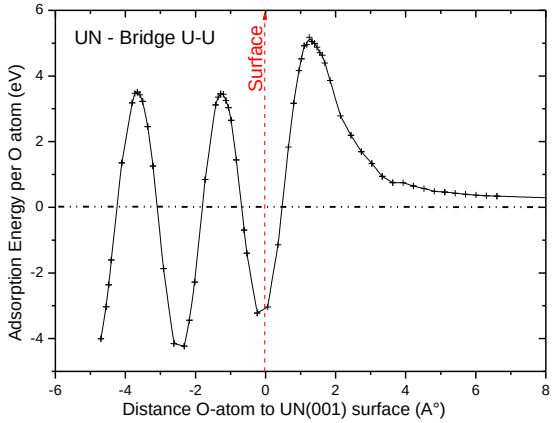

Fig. 5 – UN(001) PES O atom calculation results at the brige site U-U

We found one position on surface at around 1 Å and the incorporation of oxygen is possible at the tetrahedral sites.

For UN_2 PES study, the more favorable on surface site depend on the atoms ending the surface, we found that UN_2(001) U terminated is more favorable than N terminated surface as illustrated in figure 6 [38]. The calculations are confirmed by using the DFT + U concept.

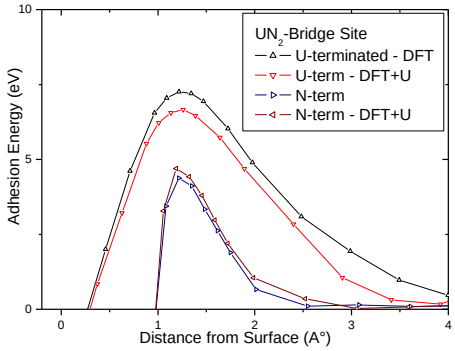

Fig. 6 – UN_2(001) U terminated and N terminated PES O atom calculation results at the bridge site

We found also, that only hollow site for UN_2(001) surface N terminated, presents character of letting the oxygen atom incorporation but adhesion energies are relatively low compared to on surface adsorptions.

4. CONCLUSION

This paper summarize DFT properties calculations of UN and UN_2; structural, mechanical and oxygen diffusion (molecular and atomic) along the (001) surfaces were performed to a comparison study. DFT and DFT + U was used since uranium 5f electrons present a strong correlation which perturb mean field theory used in classical exchange functional and then the fundamental energy is disturbed. DFT results show good agreement with experimental values for structural and mechanical data, however using the Hubbard U correction to achieve certain physical intrinsically properties (UN to become AFM and UN_2 to attain experimental cell parameter value), some properties were corrected but others have shown more deviation from experimental worth, example of UN where cell parameter become 4.91 A° instead of experimental value of 4.886, however, the bulk modulus (199 GPa) is closed to experimental value (194 GPa). Diffusion of oxygen atomic was studied for UN and UN_2 (001) surfaces, bridge site was the most favorable on surface site for the two O adsorption, but only UN show O inlay through the bridge site. We've studied Oxygen molecular diffusion around the UN (001) bridge site and UN_2(001) hollow site, by using the PES concept, the dissociation of the O_2 molecule was proved for the two structures.

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