International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:1, 2015

Physical Properties of Uranium Dinitride UN_2 by Using Density Functional Theory (DFT and DFT+U)

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***Abstract*—**Physical properties of uranium dinitride (UN_2) were investigated in detail using first principle calculations based on density functional theory (DFT). To study the strong correlation effects due to 5f uranium valence electrons, the on-site coulomb interaction correction U via the Hubbard-like term (DFT+U) was employed. The UN_2 structural, mechanical and thermodynamic properties were calculated within DFT and Various U of DFT+U approach.

The Perdew–Burke–Ernzerhof (PBE.5.2) version of the generalized gradient approximation (GGA) is used to describe the exchange-correlation with the projector-augmented wave (PAW) pseudo potentials.

A comparative study shows that results are improved by using the Hubbard formalism for a certain U value correction like the structural parameter. For some physical properties the variation versus Hubbard-U is strong like Young modulus but for others it is weakly noticeable such as bulk modulus.

We noticed also that from U=7.5 eV, elastic results don't agree with the cubic cell because of the C44 values which turn out to be negative.

Keywords*—Ab initio*, bulk modulus, DFT, DFT + U.

I. Introduction

URANIUM nitrides are considered as promising fuel materials for the generation-IV fast breeder reactors because of their phase stability and especially for the superior thermal physical properties compared to oxides fuels, indeed, better high melting point, high thermal conductivity and high metal density [1]-[3].

Standard DFT computations of uranium nitrides showed agreement results compared to experiments for several physical properties but on the other hand some other properties are far from the experimental value (example of UN which is described as ferromagnetic (FM) conductor instead of the experimentally observed anti-ferromagnetic (AFM) type [4]).

These unreasonable ground state properties are caused by the strong Coulomb correlation among the partially filled 5f electrons. Several theoretical methods have been developed to take into account this strong intra-atomic interaction among them the self-interaction correction (SIC) [5], [6] and a combination of dynamical mean field theory (DMFT) with LDA [7], [8].

In our case, we are interested in the DFT+U formalism developed by [9] which consists of adding a functional depending on the parameter U to the conventional one to force the on-site coulomb repulsion [10]-[12]. Nowadays, this method of calculation is becoming a standard technique for studying strongly correlated materials like uranium nitrides or oxides and most of actinide compounds [13], [14].

In this work, we report on a comparative study on a conventional exchange correlation functional (Projector Augmented Wave (PAW) method within the Perdew-Burke-Ernzrhof (PBE.52) Gradient Generalized Approximation (GGA)) and a DFT+U (PBE.52+U) correction calculations for uranium dinitride (UN_2) [15], [16].

Lattice parameter, electronic structure, elastic, mechanical and thermodynamic properties of uranium dinitride UN_2 were calculated within the conventional exchange functional and the Hubbard-U approach for several values of U. Our results are in good agreement with other theoretical values and the effect of the parameter U is apparent and depends on the physical property; for some aspects like Young or Shear modulus the sensitive to the U variation is important while for other characteristics like bulk modulus or energy bands the dependence is weak but noticeable.

II. Methodology and Computation

In this study, all DFT calculations were performed with the well-known Vienna Abinitio Simulation Package (VASP, version5.3) using the Exchange-correlation described by the Perdew-Burke-Ernzrhof (PBE.52) Generalized Gradient Approximation (GGA) and the projector-augmented wave (PAW) pseudo potentials, 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 [17], [18]. To evaluate correctly electronic structure of materials owning strong Coulomb correlations caused by the uranium 5f electrons, the covariant version of the DFT+U energy functional proposed by Dudarev et al was applied.

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

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 show, the total energy depends on the parameters U and J, where the difference (U-J) is meaningful.

Parameter U in DFT + U approach is a variable in our study, parameter J for uranium atom is taken equal to 0.51 eV

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as [19] has determined. In all this paper, the difference (U-J) is labeled U.

Numerous convergence study of the total energy to determine the nominally cutoff energy and the k-point grid (Monkhorst & Pack mesh method [20]) in the Brillouin zone (BZ) was done by varying these values. Cutoff energy was taken as 550 eV; k-point grid was set to 11x11x11 which ensures total energy to converge less than 10^{-4}eV per atom.

Mechanical properties such as stiffness and stability of materials can be deduced from elasticity study. To calculate the elastic constant as developed in VASP5.3, the elastic tensor is determined by performing finite distortions of the lattice and a strain-stress calculation [21].

The Born stability criteria denote the elastic stability of a solid [22], [23]. For a cubic structure, the stability criteria can be provided by:

$$C_{11}>0 ; C_{44}>0 ; C_{11}-C_{12}>0 ; (C_{11}+2C_{12})>0 ; C_{12}<B<C_{11} \quad (2)$$

UN_2 Bulk modulus is derived from two methods: bulk and elastic calculation, the first one is obtained by fitting the energy-volume data in the third-order Birch-Murnaghan equation of states (EOS) [24]. For the elastic method, Bulk modulus, shear modulus, Poisson's ratio and anisotropic factor are evaluated using the Voigt-Reuss-Hill (VRH) relations [25]-[27].

III. Results and Discussion

A. Structural Properties

UN_2 belongs to the space group $fm\bar{3}m$(No. 225), its crystalline structure follows the CaF_2-type ionic structure where the conventional cell is an FCC structure with four atoms of uranium and eight atoms of nitrogen occupying all the tetrahedral sites [28].

We calculated the total energy of UN_2 by varying the lattice constants to determine the theoretical equilibrium value for every exchange correlation functional (both conventional and varying the Hubbard-U for the DFT + U method). Results of structure parameters are reported in Table I compared to experimental and theoretical abinitio values [29]-[31].

TABLE I
Lattice Parameter Results

Method	PBE52 (this work)	Experiment	Other ab initio [28], [30], [31]
Lattice parameter	5.276	5.31	5.284, 5.259, 5.26
Cohesive energy	21.3	-	21.5, 17.9, 20.9

As can be seen from Table I, the PBE52 exchange correlation functional predicts a lattice parameter of 5.276 A° value which is in the order of magnitude of other theoretical values but slightly lower than the 5.31A° experimental value. The cohesive energy is in the magnitude of order of other theoretical results.

By varying Hubbard-U in the DFT+U approach, one can see from Fig. 1, the increase of lattice values with parameter U.

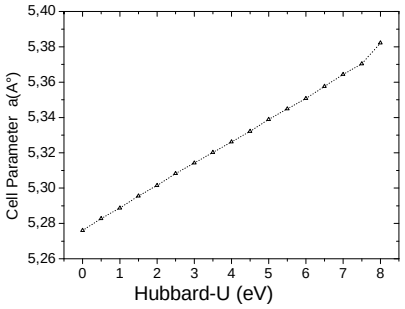

Fig. 1 UN_2 Cell parameter versus Hubbard-U parameter

From Fig. 1 and Comparing to the experimental value, the optimal Hubbard-U parameter is around a value of U_{optim}= 2.6 eV, but a range of values within [2 - 3.5] give a precision less than 0.1%.

B. Electronic Properties

The corresponding band structures were obtained with 21x21x21 k-point mesh grid for UN_2 unit cell, the Hubbard-U variations affect weakly the band structure as it is shown in Fig. 2. We remark the band gap near Fermi energy is practically the same; all the curves of several colors are superimposed.

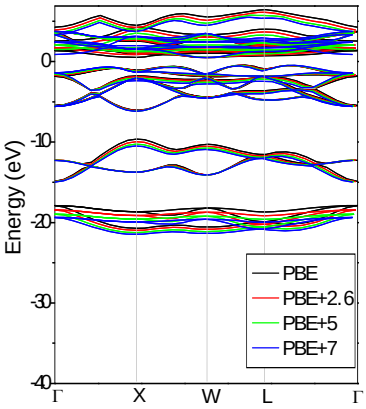

Fig. 2 UN_2 energy bands constructed for Hubbard-U = 0, 2.6, 5 and 7 eV

The band gap near the Fermi energy increase slightly from 0.72eV for Hubbard-U = 0, to 0.8eV at U=5eV, and then decrease to 0.75 for U =7eV (see Fig. 3). These values confirm the semiconducting nature of UN_2 as mentioned in [30]. For U_{optim} the band gap is 0.774 eV.

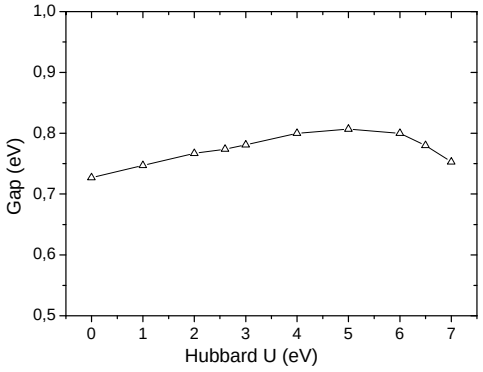

Fig. 3 UN_2gap versus Hubbard-U

C. Elastic Properties

The calculations of the elastic constants were performed using the VASP (version 5.3) within the GGA and GGA+U approach (PBE52). All the results satisfy the criteria of mechanical stability of a cubic structure provided by eq. (2), particularly, bulk modulus values are between C12 and C11 for every Hubbard-U as mentioned in Fig. 4 (UN_2 is intrinsically stable).

Since there are no corresponding experimental results so far, we report in Table II our results compared to available theoretical values performed for some values of U in which calculations were performed using DFT + U method and taking into account correction of occupation matrices.

TABLE II
ELASTIC CONSTANTS

method	PBE52+U (VASP5.3, this work) (without occupation matrices correction)			GGA+U (VASP4.6) (with occupation matrices correction)[30]		
Elastic constants	C11	C12	C44	C11	C12	C44
U=0	494.4	133.2	62.2	495.4	137.3	65.6
U=2	-	-	-	488.2	140.5	55.3
$U_{optim=2.6}$	486.3	138.3	49.6	-	-	-
U=4	482.4	141.3	41.3	483.8	146.2	41.3
U=7	470.8	141.2	5.6	-	-	-

From Table II, one can see the similitude of results between our calculations and those from [30]; the influence of the metastable states for UN_2 is then not perceptible.

We also, extend the data calculation of variation of elastic constants versus Hubbard-U from U =0 to U=10eV. We plot in Fig. 4 the Hubbard variation from 0 to 7eV because elastic results are conform to the cubic cell elastic criteria, but from U= 7.5 eV to U=10eV, the C44 becomes negative value (not plotted).

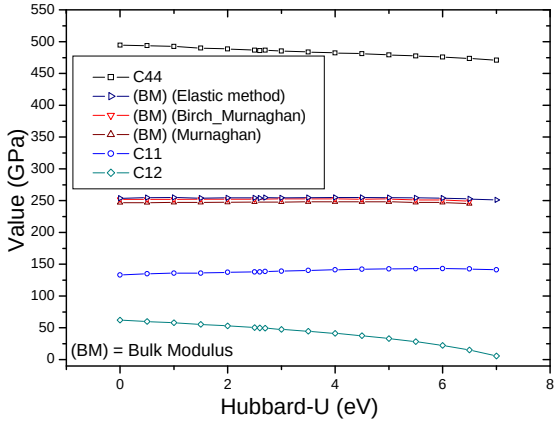

Fig. 4 UN_2 elastic constants and bulk modulus vs Hubbard-U

D. Mechanical Properties

Mechanical properties were determined using EOS or VRH relations for a Hubbard-U variation. Compared to other theoretical values, see Table III, our values are in good agreement and one can remark the Hubbard-U effect on results.

TABLE III
MECHANICAL VALUE

	PBE52+U (this work)					
U (eV)	B(EOS) (GPa)	B (GPa)	G (GPa)	E (GPa)	γ	A
U=0	251.9	253.6	97.0	258.0	0.330	0.344
U=2	252.4	-	-	-	-	-
$U_{optim=2.6}$	252.5	254.0	84.5	228.1	0.350	0.285
U=4	252.8	255.0	76.1	207.7	0.364	0.242
	Reference [30]					
U=0	-	256.7	99.4	264.2	0.328	0.366
U=2	253.5	256.4	89.4	240.2	0.344	0.318
U=4	-	258.7	75.7	207.0	0.367	0.245

The bulk modulus is relatively stable (vs Hubbard-U) for both EOS and elastic method, nevertheless Birch-Murnaghan values are close to the elastic ones, meanwhile the relatively larger value of UN_2 bulk modulus (around 250 GPa) compared to UN (194 GPA), UO_2 (207 GPa) or UC_2 (216 GPa) showed better resistance to fracture. Fig. 5 shows the evolution of derivative bulk modulus vs Hubbard-U for the two EOS Murnaghan and Birch-Murnaghan methods [32]-[34].

The variation of shear modulus against amplifying Hubbard-U value is noticeable, from G=97.0 GPa for U=0 to G=39.3GPa for U=7.0. Nevertheless, all UN_2 G/B ratios (G/B indicates the malleability measure of polycrystalline materials as proposed by an empirical method described in [35]) vary from 0.38 to 0.16, values which are less than the nominal value 0.5 which means that UN_2 behaves in a ductile manner (otherwise, if G/B > 0.5 the material demonstrates brittleness).

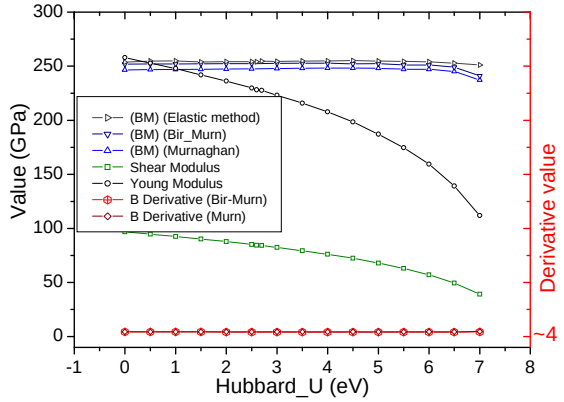

Fig. 5 UN_2 mechanical value versus Hubbard-U

E. Thermodynamic Properties

We employed the Hellmann–Feynman theorem and the direct method to calculate the phonon density of state and the thermodynamics parameters of UN_2 [27].

The 5x5x5Monkhorst-Pack k-point schemes are used for a 2x2x2 UN_2 supercell with18 U and 36 N atoms.

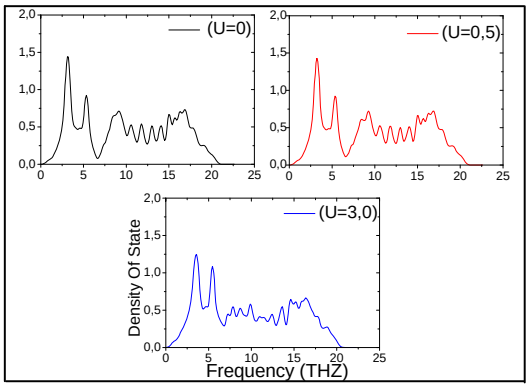

Fig. 6 UN_2Phonon density of state (DOS) using PBE (U=0) and PBE + U (U=0.5 and 3)

The total and projected phonon DOS for UN_2 are plotted in Fig. 6 for Hubbard-U = 0, 0.5 and 3.0 eV. The curves are nearly the same. Since the uranium atom is heavier than nitride atom, the phonon DOS is split into two parts as illustrated in Fig. 6, from 0 to around 6.7 THz the vibrations of uranium atoms are dominant and then up to 21 THZ the vibrations mainly come from nitride atoms.

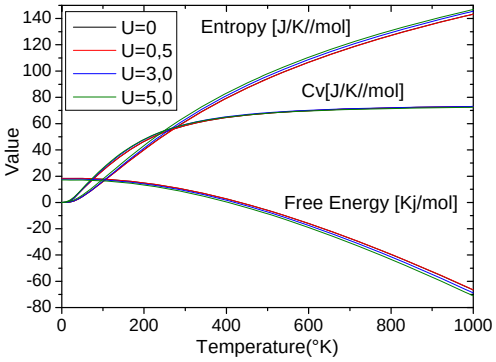

Fig. 7 UN_2 Thermodynamic properties using PBE (U=0) and PBE+(U=0.5, 3, 5)

The thermodynamical quantities such as the Free energy, Entropy, and specific heat are calculated using phonopy code within GGA and GGA + (U=0.5, 3 and 5) approaches [36]. A light deviation of results is perceptible for the values of the free energy and entropy by increasing the Hubbard-U (see Fig. 7), but not noticeable for the values of heat capacity which are in the same order of magnitude of theoretical approaches [37].

IV. Conclusion

Physical properties of uranium dinitride (UN_2) were evaluated using a conventional exchange correlation functional (Projector Augmented Wave (PAW) method within the Perdew-Burke-Ernzrhof (PBE.52) Generalized Approximation (GGA) and the covariant version of the DFT+U energy functional proposed by [9]. The study was performed without monitoring the occupancy matrices. All our results, concerning the structural, elastic or thermodynamic study are in the same magnitude order compared to *ab initio* theoretical and experimental values. In fact, the nonmagnetic nature of UN_2 was confirmed for the GGA and the GGA+U approach. The equilibrium lattice constant of UN_2 obtained with GGA method gives a value less than the experimental value as predicted, nevertheless by correcting the exchange functional with the Hubbard-U value (DFT+U); the lattice parameter approach the experimental result by increasing U until an optimal U_{optim} =2.6 eV (a=5.31A°). Other physical parameters were then calculated versus Hubbard-U values with a stress to the values obtained with the value of U_{optim}. The semi conducting nature of UN_2 was proved and the band gap = 0.75eV evaluated for U_{optim} =2.6 doesn't show a considerable divergence by varying Hubbard-U values. Elastic and mechanical properties of UN_2 show a small dependence versus Hubbard-U value with the exception of the C44 parameter and young modulus, nevertheless practically, the variety of all elastic and mechanical values become large by growing the Hubbard-U value from 5.5 eV. Total projected phonon density of state DOS and thermodynamic results don't show a large deviation by raising the Hubbard-U especially for the heat capacity.

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