



Communication

Nitrogen non-stoichiometric stabilization of UN₂Kingsley Onyebuchi Obodo^{a,b}, Moritz Braun^a^a Physics Department, University of South Africa, P.O. Box 392, 0003 Pretoria, South Africa^b Physics Department, University of Pretoria, Pretoria 0002, South Africa

ARTICLE INFO

Communicated by F. Peeters

ABSTRACT

Ab initio quantum chemical calculations are employed to investigate the electronic, mechanical, elastic and thermodynamic properties of UN₂. The influence of nitrogen non-stoichiometry on the electronic, structural and dynamical properties of cubic uranium dinitride (UN₂) is evaluated. The equilibrium lattice parameters, electronic band structure, density of state (DOS), elastic properties and phonon frequencies for the UN_{2-x} (where $x=0, 0.125, 0.25, 0.5$) compounds are determined and analyzed in comparison with available experimental data. The introduction of nitrogen vacancies in UN₂ structure is accompanied by pronounced DOS changes due to the shifting of the various electronic orbitals as well as the appearance of novel vacancy states in the near-Fermi region. We find that UN_{1.75}, which is a 12.5% nitrogen deficient structure, is observed to be dynamically and elastically stable in good agreement with experimental observations.

1. Introduction

Actinide based nitride compounds have unique, complex and interesting properties, which are the subject of continuous theoretical and experimental investigations [1–8]. These properties are caused mainly by the presence of partially filled 5*f* orbitals, that give rise to strong electron–electron interactions, and the large number of electrons that results in heavy fermionic effects.

It has been realized that the electron–electron interactions in the partially filled 5*f* orbitals cannot be properly described using local density approximation (LDA) and generalized gradient approximation (GGA) exchange correlation functionals. The shortcomings of the above-mentioned functionals can be overcome using various approaches such as the self-interaction correction (SIC), DFT hybrid approach, DFT+*U*, GW, etc. The DFT+*U* (LDA+*U* or GGA+*U*) methodology effectively corrects a number of the deficiencies observed in this class of materials concerning their band gap [9–11], hence it is used to resolve this problem. This implies that accounting for the 5*f* electrons is essential for most of the early actinide compounds. Worth noting is that, irrespective of the underlying basis in estimating the *U* parameter, it still remains an *ad hoc* parameter.

The uranium-based nitrides are a class of ceramic materials. They comprise uranium mononitride (UN), uranium sesquinitride (U₂N₃) and uranium dinitride (UN₂). Here nitrogen having a –3 oxidation state is bounded to uranium metal. From both a scientific and technological point of view, the understanding of uranium-based

nitride is of significant interest [12,13]. Scientifically, it provides the avenue for an in-depth understanding of the electron–electron interactions in this class of compounds. Technologically, it provides a means for clean and safe energy generation at a competitive cost. Based on the significance of these uranium nitrides from both a scientific and technological point of view, the understanding of the electronic and structural properties is essential to effectively harness, control, and optimally utilize these materials.

Evarestov et al. [14] investigated the electronic structure of crystalline UN, U₂N₃ and UN₂. However, they did not consider the dynamic stability of these compounds. Recently, we showed [3] that most of the early actinide dinitride compounds (ThN₂, PaN₂, NpN₂ and PuN₂) are stoichiometric compounds, as well as thermodynamically stable. A notable exception was UN₂ that exhibits some degree of instability, which is clearly observed in the phonon dispersion plot. Our theoretical observation is in line with the experimental studies dating back to the 1970's by Rundle et al. [15], Tagawa et al. [16,17] and Silva et al. [18]. Recent experimental evidence by Poineau et al. [8] in 2012 showed that a stoichiometric compound of UN₂ cannot be synthesized. Long et al. [19,20] also investigated the electronic structure of U₂N₃ using both experimental and theoretical methods. The various experimental observations show that the correct description for the non-stoichiometric UN₂ structure may be between UN_{1.75} and UN_{1.78}. The CaF structure was hypothetically assigned to the uranium dinitride compound on the basis of experimental data from the actinide dinitrides with N/U=1.75–1.78. The assertion is that the non-stoichiometry

E-mail addresses: obodoko@unisa.ac.za (K.O. Obodo), braunm@unisa.ac.za (M. Braun).<http://dx.doi.org/10.1016/j.ssc.2017.01.009>

Received 2 December 2016; Received in revised form 9 January 2017; Accepted 13 January 2017

Available online 17 January 2017

0038-1098/ © 2017 Published by Elsevier Ltd.

arises from the presence of nitrogen vacancies in UN_2 . Therefore, we investigate the influence of nitrogen non-stoichiometry on the electronic and mechanical properties of uranium dinitride compound to properly elucidate the stability of the structure and understand the physics of this nitride. Various degree of nitrogen vacancies are introduced into UN_2 compound in the ferromagnetic fluorite structure to understand the reason behind stoichiometric UN_2 instability.

A detailed first principles study on the nitrogen non-stoichiometric stabilization of UN_{2-x} structures (where $x=0, 0.125, 0.25, 0.5$) using the density functional theory approach within the generalized gradient approximation for the exchange-correlation potential plus the Hubbard U (GGA + U) with spin polarization (SP) and spin-orbit coupling (SOC) as implemented in the Vienna *Ab-initio* simulation package (VASP) is lacking. We calculate the electronic, elastic, structural and dynamic properties of these compounds. Overall, we show that a non-stoichiometric structure of UN_2 is stabilized from a purely quantum-mechanical based calculation. The presence of meta-stable and different magnetic configuration with respect to the Hubbard U are not considered in this current communication.

A brief description of the computational methodology used to analyze the structural and electronic properties of UN_{2-x} structures is presented in Section 2. The details of the UN_{2-x} structures are presented in Section 3. In Section 4, we discuss the effect of the various nitrogen vacancies on the electronic band structure, elastic properties, charge density distribution and phonon frequencies on these structures. Finally, we summarize our conclusions in Section 7.

2. Methodology

All the electronic, structural, elastic and dynamics computations were performed using density functional theory [21] as implemented in the VASP code [22]. The electron wave functions of the uranium and nitrogen atoms are described using the projector augmented wave (PAW) method of Blöchl in the implementation of Kresse and Joubert [23]. The PBE [24] form of the GGA exchange-correlation potentials is used together with its GGA + U variants. The Hubbard- U parameter of 2 eV for the onsite correlation energy was taken from our previous studies on the structure of actinide dinitrides [3]. It was determined by optimizing the lattice parameter with respect to the U . An adequately converged kinetic energy cutoff of 550 eV was chosen to ensure fully converged total energies for the uranium nitride structures. A spacing of \mathbf{k} -points of 0.2 \AA^{-1} for the Monkhorst-Pack [25] grid is used to sample the Brillouin zone, and Methfessel–Paxton smearing [26] with a width of 0.2 eV was used to integrate over the bands at the Fermi level. The unit cell parameters and atomic positions are optimized with an energy and force tolerance of 10^{-7} eV and 10^{-4} \AA/eV respectively. The total energy, electronic band structure and density of states (DOS) were calculated using the tetrahedron integration method with Blöchl corrections. The ferromagnetic (FM) spin polarized configuration was considered.

A method employing a least-squares fit [27], as implemented in the MedeA-MT module is used to determine the elastic properties (bulk, shear and Young's moduli). The MedeA-MT module also uses the tetrahedron method for the Brillouin zone integrations. The elastic properties are calculated from the Hill values using the MedeA-MT, which are a geometric mean of the Voigt and Reuss values. The eigenvalues of the stiffness matrix give an indication of the mechanical stability of the structures under consideration, which is used to obtain the elastic constants. The Hill values [28] are used in the estimation of longitudinal, shear and mean sound velocities, and the Debye temperatures [29].

The MedeA PHONON package [30] is used to determine the phonon dispersion and phonon densities of states. It was also applied during the execution of the individual normal modes of vibration for the computation of the atom trajectories. The symmetry analysis of the

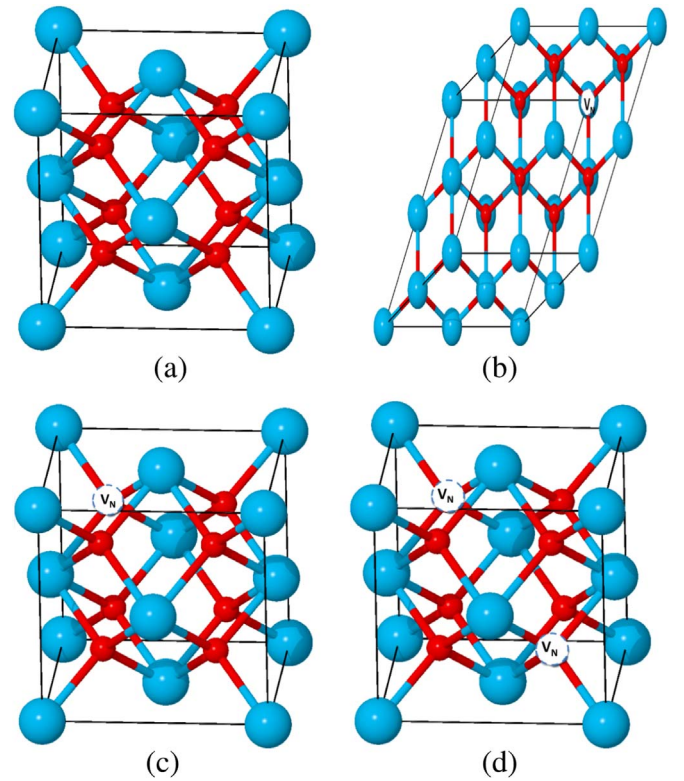


Fig. 1. (Color online) The crystallographic unit cells of the various uranium nitride structures UN_{2-x} considered (a) UN_2 , (b) $\text{UN}_{1.875}$, (c) $\text{UN}_{1.75}$ and (d) $\text{UN}_{1.5}$. Blue spheres depict uranium atoms, the red spheres depict the nitrogen atoms and the white spheres with V_N indicates a missing nitrogen atom.

modes of vibration for the contents of the spectroscopic unit cell is provided by the software and follows the usual prescriptions of symmetry theory. We have shown previously that the influence of the Hubbard U parameter is negligible on the phonon frequencies for the early actinide based nitrides [3]. Therefore, we have only presented results for the phonon frequencies within the DFT (GGA) approximation.

3. Structures

A precise prescription for the structural determination would require a uniformly large super cell size of approximately 64–128 atoms. Subsequently, different nitrogen vacancies would be introduced. Followed by the estimation of the lowest energy structure, which would be used to determine the specific UN_{2-x} structure of interest. However, this procedure is not tractable as the permutations for each structure would be highly computationally intensive. A tractable and concise approach was to consider the smallest super cell size with the lowest energy for each non-stoichiometric structure.

Fig. 1 shows the various nitrogen non-stoichiometric UN_{2-x} crystal structures considered. In Fig. 1a, the stoichiometric fluorite UN_2 structure is presented. It is known to possess an underlying cubic motif with the $Fm-3m$ space group. The experimental and calculated lattice parameter within GGA + U for UN_2 are 5.308 Å [15] and 5.302 Å respectively. Fig. 1b shows the $\text{UN}_{1.875}$ supercell structure, which consists of a $(2 \times 2 \times 2)$ primitive unit cell of UN_2 with a total of 23 atoms (8 uranium and 15 nitrogen atoms). $\text{UN}_{1.875}$ is 6.25% nitrogen deficient compared to UN_2 . Fig. 1c shows the $\text{UN}_{1.75}$ supercell structure, which consists of a UN_2 in the fluorite structure with a total of 11 atoms (4 uranium and 7 nitrogen atoms). $\text{UN}_{1.75}$ is 12.5% nitrogen deficient compared to UN_2 . Fig. 1d shows the $\text{UN}_{1.5}$ supercell structure, which consists of a UN_2 in the fluorite structure with a total of 10 atoms (4 uranium and 6 nitrogen atoms). $\text{UN}_{1.5}$ is 25% nitrogen deficient

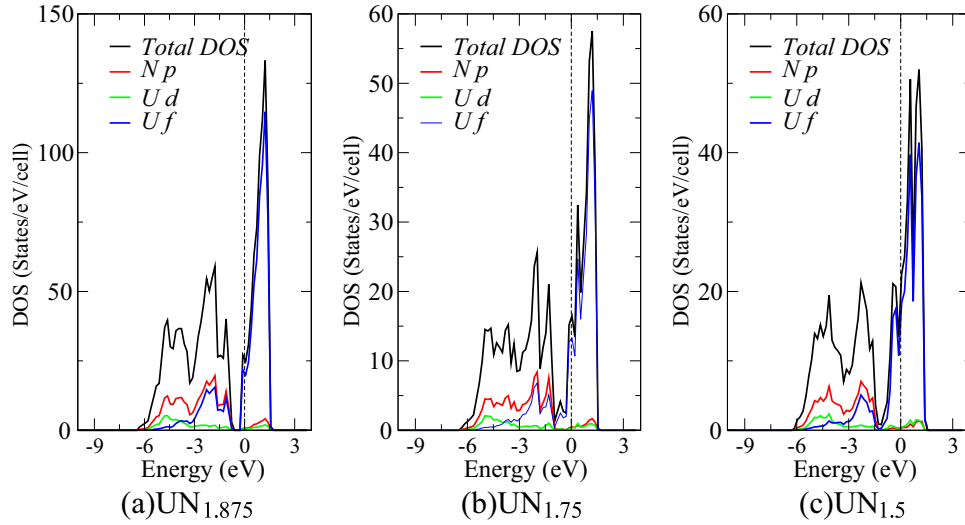


Fig. 2. (Color online) The computed total and projected densities of states (PDOS) for (a) $\text{UN}_{1.875}$ (b) $\text{UN}_{1.75}$ (c) $\text{UN}_{1.5}$ within the description of the GGA + U ($U=2$ eV). The Fermi energy level is set at zero and is represented using dashed line.

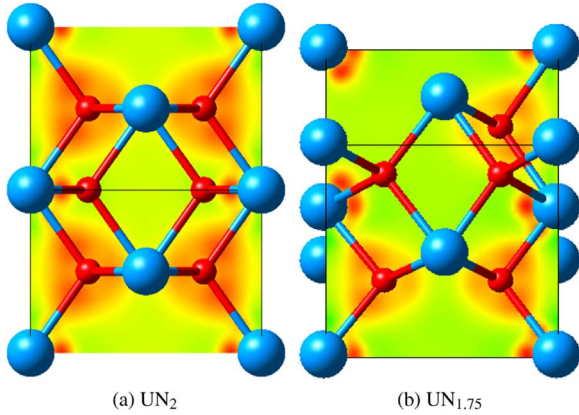


Fig. 3. (Color online) Contour map of plane-averaged charge density distribution for (a) UN_2 and (b) $\text{UN}_{1.75}$.

compared to UN_2 . The structure is determined by taking symmetry constraints into account and subsequently determining the minimum energy configuration. Fig. 1d, which is relatively metastable compared to α or β - U_2N_3 structure is considered to ensure uniformity. All the structures have an underlying cubic symmetry. Further explanation is provided in Section 6.

4. Electronic properties

To understand the influence of non-stoichiometric nitrogen on the various UN_{2-x} based structure, we investigate the electronic properties of these structures.

An insulating character with a band gap ranging from about 0.83 eV [3] using GGA+ U (with a Hubbard U of 2 eV) to 0.94 eV using the all electron [31] approach has been observed from various studies carried out on UN_2 to understand its quantum mechanical properties. These studies demonstrate that the electronic properties of UN_2 are governed mainly by the 5f states, while the top of the valence band (VB) and bottom of the conduction band (CB) are largely characterized by the hybridization of the U 5f and N 2p states.

Fig. 2 shows the computed electronic total density of states (DOS) and projected densities of states (PDOS) for the various non-stoichiometric UN_2 structures investigated in this current study. The DOS provides an indication of how closely packed the electronic energy levels are distributed within the energy interval. Furthermore, the atomic projections of the uranium p , d , and f states along with the

nitrogen 2p states are given to elucidate their individual electronic signature. In Fig. 2a, the metallicity of $\text{UN}_{1.875}$ results largely from the shift in the 5f electrons in the bottom of the CB in stoichiometric UN_2 into the Fermi level. Fig. 2b shows metallic $\text{UN}_{1.75}$, which is dominated by the 5f electrons. Furthermore, Fig. 2c shows metallic character with the Fermi level dominated by the 5f electrons. This observation is in line with our previous investigation on stoichiometric UN_2 [3] that the uranium 5f electrons primarily characterize the system. The general features of the energy bands are metallic for the non-stoichiometric structures investigated. The metallicity of these structures from a purely computational point of view is attributed to the presence of various degree of nitrogen vacancy, which results in extra bonding states.

Worth noting is the influence of spin-orbit coupling in the accurate qualitative description of heavy elements as demonstrated in our previous studies [32,3]. For the various non-stoichiometric alloys considered in this investigation, half-metallicity is obtained taking into account only the presence of magnetization. However, the inclusion of SOC results in metallic structures with zero total magnetization. Recent experimental studies confirm our theoretical prediction that the UN_{2-x} systems are metallic structures [20].

Fig. 3a and b shows the contour map of plane-averaged charge density distributions along the (011) plane of the stoichiometric UN_2 and non-stoichiometric $\text{UN}_{1.75}$ crystal structures. The charge density distributions are presented as a superposition on the ball-and-stick representation of the corresponding structural model. The charge density distribution for the two structures are presented to show the influence of atomic vacancy on the UN_2 lattice. Fig. 3a and b shows that the charge density localization along the U–N bond length is non-uniform. It has maxima at both U and N atomic centers but progressively decreases towards the bond center, with the global minimum localized at hollow sites. The concentration of the charge density shifts towards the nitrogen atom along the U–N bond. We ascribe this uranium-to-nitrogen charge transfer in the fluorite UN_{2-x} compound to nitrogen being more electronegative than uranium. Therefore, the U–N bonds show strong ionic character with weak covalent character. Furthermore, the only observed difference in the charge density distribution of Fig. 3a and b is charge depletion around the nitrogen vacancy region which is attributed to the missing atom. For more in-depth analysis of these structures, we now evaluate their elastic properties.

Table 1

The bulk, shear and Young's moduli (calculated from Hill values in GPa), acoustic velocities (in m s^{-1}) and Debye temperature (K) using GGA+ U within the SOC scheme with a Hubbard U of 2 eV.

| Compound | B_H | G_H | Y_H | v_s | v_l | v_m | θ_D |
|---------------------|--------|-------|--------|-------|-------|-------|------------|
| $\text{UN}_{1.5}$ | 138.19 | 49.71 | 131.87 | 2116 | 4292 | 2376 | 283.7 |
| $\text{UN}_{1.75}$ | 199.67 | 89.96 | 234.44 | 2791 | 5261 | 3119 | 387.8 |
| $\text{UN}_{1.875}$ | 228.97 | 95.12 | 250.53 | 2853 | 5517 | 3194 | 403.7 |
| UN_2 | 251.71 | 89.71 | 238.96 | 3740 | 5585 | 3078 | 396.0 |

5. Elastic properties

Table 1 shows the calculated elastic properties of the various UN_{2-x} compounds considered with a Hubbard U parameter of 2 eV. This allows for consistency and comparison of all the UN_{2-x} structures. The inclusion of the U parameter results in better agreement of the calculated elastic properties with other available theoretical and experimental data. The calculated bulk, shear and Young's moduli for the structures are positive definite, which are determined from their elastic constants. This indicates that the structures are all elastically stable. Note that the elastic stability is related to sum rules. Therefore, negative elastic constants do not necessarily signify elastic instability. The elastic properties determined for UN_2 , $\text{UN}_{1.875}$ and $\text{UN}_{1.75}$ are all comparable. From the calculated values of shear (transverse) velocity and longitudinal velocity, we determine the mean velocity. The mean velocity is used to determine the Debye temperature (θ_D), which gives an indication of the material stiffness. $\text{UN}_{1.75}$, $\text{UN}_{1.875}$ and UN_2 have numerically similar stiffness compared to $\text{UN}_{1.5}$, which can form as a stoichiometric compound with chemical formula U_2N_3 . However, the calculated Debye temperature for the various structures does not follow a linear trend. Hence, we evaluate the phonon modes to determine their dynamic stability.

6. Phonon dispersion

Our previous investigation of actinide-based nitrides shows the presence of imaginary phonon frequency in stoichiometric UN_2 [3]. The theoretical findings are in agreement with experimental results corroborating the non-stoichiometric nature of UN_2 compound. As mentioned earlier, the presence of nitrogen vacancies in UN_2 could lead to dynamic stabilization of the compound. However, we applied various degree of isotropic pressure to stoichiometric UN_2 structure with the aim of structural stabilization. The imaginary phonon modes remained with no stabilization or phase transition with pressure. A number of factors could be responsible such as unit cell size, actual number of atoms, huge energy barriers, etc. However, these factors were not explored further due to computational constraints. Next, the effect of nitrogen non-stoichiometry on the phonon modes of UN_{2-x} structures are investigated to determine the possibility of structural stabilization.

Fig. 4 shows the phonon dispersion plot for non-stoichiometric $\text{UN}_{1.5}$ structure. We observe imaginary phonon modes (negative phonon frequency) around the Γ -point. This indicates that the non-stoichiometric $\text{UN}_{1.5}$ structure is dynamically unstable. The slight imaginary phonon modes might be suggestive of a metastable structure, which have a likelihood of structural transformation to the stoichiometric $\alpha\text{-U}_2\text{N}_3$ or $\beta\text{-U}_2\text{N}_3$ structure rather than the defective considered $\text{UN}_{1.5}$ structure under certain conditions, which are beyond the scope of the current investigation [20]. Uranium atoms govern the dynamics of the low lying frequency, hence, they contribute solely to the imaginary modes. In addition, the nitrogen atoms govern the dynamics of the higher lying frequencies, which are much lighter than the uranium atoms. The proportion of the nitrogen vacancies in the non-stoichiometric $\text{UN}_{1.5}$ structure is relatively large, hence, dynamic stabilization is not achieved.

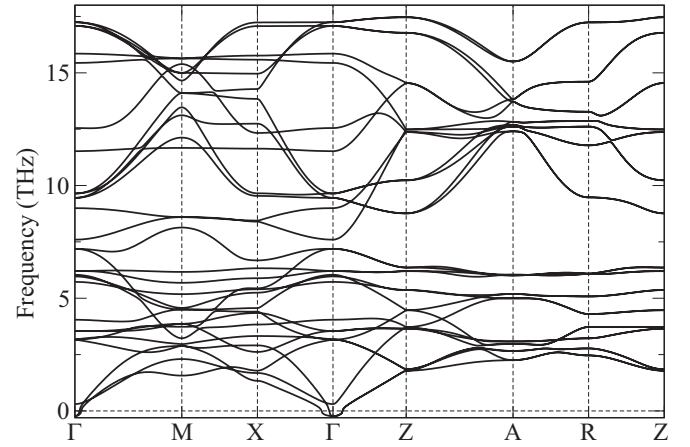


Fig. 4. The phonon dispersion plot of $\text{UN}_{1.5}$ structure showing the lattice dynamics of U and N atoms. Note the presence of imaginary (negative) phonon frequencies at the Γ -point demonstrating structural instability.

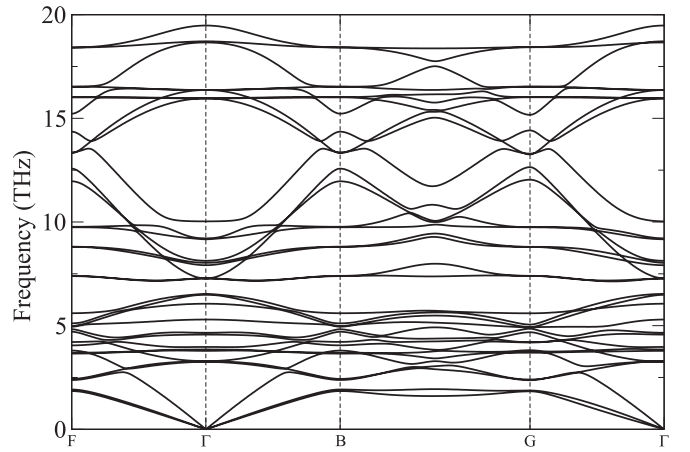


Fig. 5. The phonon dispersion plot of $\text{UN}_{1.75}$, showing the lattice dynamics of U and N atoms.

In Fig. 5, we observed no imaginary phonon modes in the phonon dispersion plot of the non-stoichiometric $\text{UN}_{1.75}$ structure. This implies that the structure is dynamically stable. As mentioned above the uranium atoms govern the dynamics of the low-lying frequencies, whereas the nitrogen atoms govern those of the higher lying frequencies. Hence, the introduction of 12.5% nitrogen vacancies in the UN_2 structure results in its dynamic stabilization.

Fig. 6 shows the phonon dispersion plot for non-stoichiometric $\text{UN}_{1.875}$ structure. Several imaginary phonon frequencies are observed at different high symmetry points. This implies that the structure is unstable. The presence of imaginary frequencies in Fig. 6 is attributed to the constrained dynamics of the uranium atoms, which govern the low-lying frequencies. The minute proportion of nitrogen vacancies in the non-stoichiometric $\text{UN}_{1.875}$ structure (which is 6.25% compared to the UN_2 structure) constrains the phonon dynamics of uranium atoms in the $\text{UN}_{1.875}$ structure resulting in the instability.

It is worth noting that the presence of nitrogen vacancies in the UN_2 structure allows for increased mobility of the uranium atom leading to reduction in the imaginary phonon frequency. In essence, this structure needs a certain amount of nitrogen vacancy to attain dynamic and elastic stability.

7. Conclusions

The structural, mechanical and electronic properties of nitrogen non-stoichiometric UN_{2-x} have been studied within the DFT approach.

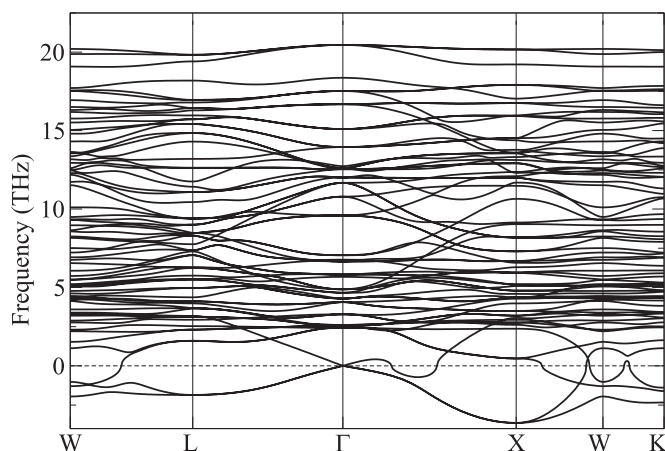


Fig. 6. The phonon dispersion plot of $\text{UN}_{1.875}$, showing the lattice dynamics of U and N atoms. Note the presence of imaginary (negative) phonon frequencies demonstrating structural instability.

Previous studies [3,32] demonstrated that for these heavy elements without taking into account the spin–orbit interactions, we would obtain a qualitative incorrect description. Within this scheme, we derive that only the $\text{UN}_{1.75}$ structure is dynamically stable as shown by the phonon dispersion data. The UN_{2-x} based compounds are elastically stable. For all the non-stoichiometric alloys investigated, half-metallicity is obtained taking into account only the presence of magnetization (SP). However the inclusion of SOC gives metallic structures. Generally, the calculated DOS show significant uranium d and f states hybridization with the nitrogen $2p$ in the UN based compound. Our current theoretical prediction is in line with previous experimental data, which proposes that certain percentage of nitrogen vacancy in the vicinity of (12.5–15%) is needed to stabilize UN_2 structure resulting in a nitrogen non-stoichiometric structure.

Acknowledgments

The authors thank National Research Foundation, University of Pretoria and University of South Africa for financial support. K.O.O. is grateful to Prof. Nithaya Chetty and Dr. Joshua T. Obodo for useful discussion.

References

- [1] Yujuan Zhang, Jianhui Lan, Qunyan Wu, Congzhi Wang, Tao Bo, Zhifang Chai, Weiqun Shi, Theoretical investigation on the solution behaviors of Ba and Zr in uranium dinitride, *Sci. China Chem.* 58 (12) (2015) 1891–1897.
- [2] K.O. Obodo, N. Chetty, Ab initio studies of Th_3N_4 , Th_2N_3 and $\text{Th}_2\text{N}_2(\text{NH})$, *Solid State Commun.* 193 (September) (2014) 41–44.
- [3] K.O. Obodo, N. Chetty, GGA+U studies of the early actinide mononitrides and dinitrides, *J. Nucl. Mater.* 442 (November (1–3)) (2013) 235–244.
- [4] K.O. Obodo, N. Chetty, A theoretical study of thorium titanium-based alloys, *J. Nucl. Mater.* 440 (May) (2013) 229–235.
- [5] V.G. Baranov, Yu N. Devyatko, A.V. Tenishev, A.V. Khlynov, O.V. Khomyakov, A physical model for evaluating uranium nitride specific heat, *J. Nucl. Mater.* 434 (2013) 248–251.
- [6] Kezhao Liu, Ren Bin, Hong Xiao, Zhong Long, Zhanglian Hong, Hui Yang, Sheng Wu, Applied Surface Science Structural analysis of nitride layer formed on uranium metal by glow plasma surface nitriding, *Appl. Surf. Sci.* 265 (2013) 389–392.
- [7] Shin-ichi Fujimori, Takuo Ohkouchi, Tetsuo Okane, Yuji Saitoh, Atsushi Fujimori, Hiroshi Yamagami, Yoshinori Haga, Etsuji Yamamoto, Yoshichika Onuki, Itinerant nature of U 5f states in uranium mononitride revealed by angle-resolved photoelectron spectroscopy, *Phys. Rev. B* 86 (23) (2012) 235108.
- [8] Frederic Poineau, Charles B. Yeamans, X-ray absorption fine structure spectroscopic study of uranium nitrides, *J. Radioanal. Nucl. Chem.* 292 (3) (2012) 989–994.
- [9] Vladimir I. Anisimov, Jan Zaanen, Ole K. Andersen, Band theory and Mott insulators: Hubbard U instead of Stoner I, *Phys. Rev. B* 44 (3) (1991) 943–954.
- [10] A.I. Liechtenstein, V.I. Anisimov, J. Zaanen, Density-functional theory and strong interactions: orbital ordering in Mott–Hubbard insulators, *Phys. Rev. B* 52 (8) (1995) R5467–R5471.
- [11] V.I. Anisimov, F. Aryasetiawan, A.I. Liechtenstein, First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA + U method, *J. Phys.: Condens. Matter* 767 (1997) 767–808.
- [12] Antoine Classie, Marco Klipfel, Niclas Lindbom, Michel Freyss, Pär Olsson, A comparison of the U-ramping and occupation matrix schemes and incorporation energies of fission products, *J. Nucl. Mater.* 478 (2016) 119–124.
- [13] Zhi-Gang Mei, Marius Stan, Pressure-induced phase transitions in UN A density functional theory study, *J. Alloys Compd.* 588 (2014) 648–653.
- [14] R.A. Evarestov, A.I. Panin, A.V. Bandura, M.V. Losev, Electronic structure of crystalline uranium nitrides UN, U₂N₃ and UN₂: LCAO calculations with the basis set optimization, *J. Phys.: Conf. Ser.* 117 (012015) (2008) 1–8.
- [15] R.E. Rundle, N.C. Baenziger, A.S. Wilson, R.A. McDonald, The structures of the carbides, nitrides and oxides of uranium, *J. Am. Chem. Soc.* 70 (1) (1948) 99–105.
- [16] Hiroaki Tagawa, Phase relations and thermodynamic properties of the uranium–nitrogen system, *J. Nucl. Mater.* 51 (1974) 78–89.
- [17] Hiroaki Tagawa, Norio Masaki, X-ray and density studies of nonstoichiometric uranium sesquinitride, *J. Inorg. Nucl. Chem.* 36 (1974) 1099–1103.
- [18] G.W. Chinthaka Silva, Charles B. Yeamans, Alfred P. Sattelberger, Thomas Hartmann, Gary S. Cereface, Kenneth R. Czerwinski, Reaction sequence and kinetics of uranium nitride decomposition, *Inorg. Chem.* 48 (22) (2009) 10635–10642.
- [19] Zhong Long, Yin Hu, Lin Chen, Lizhu Luo, Kezhao Liu, Xinchun Lai, UN_{2-x} layer formed on uranium metal by glow plasma nitriding, *J. Alloys Compd.* 620 (2015) 289–293.
- [20] Zhong Long, Lizhu Luo, Yong Lu, Yong Hu, Kezhao Liu, Xinchun Lai, Study on the electronic structure of $\alpha\text{-U}_2\text{N}_3$ by XPS and first principles, *J. Alloys Compd.* 664 (2016) 745–749.
- [21] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (3B) (1964) 864.
- [22] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54(16) (1996) 11169 (18).
- [23] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (3) (1999) 1758–1775.
- [24] John P. Perdew, Kieron Burke, Matthias Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (18) (1996) 3865.
- [25] Hendrik J. Monkhorst, James D. Pack, Special points for Brillouin-zone integration, *Phys. Rev. B* 13 (12) (1976) 5188–5192.
- [26] Methfessel Chauhan, A.T. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Phys. Rev. B* 40 (6) (1989) 3616.
- [27] Yvon Le Page, Paul Saxe, Symmetry-general least-squares extraction of elastic data for strained materials from ab initio calculations of stress, *Phys. Rev. B* 65(10) (2002) 104104(14).
- [28] R. Hill, The elastic behaviour of a crystalline aggregate, *Proc. Phys. Soc. Sect. A* 65 (5) (1952) 349–354.
- [29] Orson L. Anderson, A simplified method for calculating the Debye temperature from elastic constants, *J. Phys. Chem. Solids* 24 (1963) 909–917.
- [30] K Parilinski, Z. Li, Y. Kawazoe, First-principles determination of the soft mode in cubic ZrO_2 , *Phys. Rev. Lett.* 78(21) (1997) 4063(4).
- [31] Philippe F. Weck, Eunja Kim, Naduvalath Balakrishnan, Charles B. Yeamans, Kenneth R. Czerwinski, First-principles study of single-crystal uranium mono- and dinitride, *Chem. Phys. Lett.* 443 (2007) 82–86.
- [32] K.O. Obodo, N. Chetty, First principles LDA + U and GGA + U study of protactinium and protactinium oxides: dependence on the effective U parameter, *J. Phys.: Condens. Matter* 25 (April) (2013) 145603(12).