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First-principles study of single-crystal uranium mono- and dinitride

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Abstract

We report all-electron relativistic calculations of the electronic and thermodynamic properties of perfect stoichiometric UN and UN₂ single crystals using the spin-polarized density functional theory. The calculated lattice parameters and interatomic distances of the relaxed unit cells are in very good agreement with recent extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD) data. Densities of states and molecular orbitals show the importance of d–f hybridization and p-orbital contributions in the valence band of UN and UN₂, respectively, while f-orbital character dominates the conduction band of both compounds. The heat capacity of UN derived from the present calculations reproduces calorimetric data within 4% up to 1000 K.

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1. Introduction

Uranium nitrides have been extensively studied experimentally since the 1960s owing to their potential applications as advanced nuclear fuels [1–3]. Their high melting point, density, and thermal conductivity are particularly attractive for future fast reactors considered by the international Forum Generation IV [4]. This explains partially the unprecedented research effort witnessed currently in uranium/first-row elements molecular chemistry [5]. Experimental studies have also revealed unusual and exciting structural and reactivity features, and raised a number of fundamental questions about the electronic structure and thermodynamic stability of uranium nitride systems [6,7].

In contrast to the wealth of experimental data available, relatively few first-principles results have been reported so far on uranium nitrides [8–11]. One of the most recent stud-

ies focused on point-defect modelling in uranium nitride crystals using two different plane-wave basis set implementations of the density functional theory (DFT) [11]. Significant discrepancies between both sets of calculations appeared in the calculated lattice constants and densities of states of pure uranium nitride crystals. These differences were ascribed essentially to the different pseudopotentials used in the two DFT implementations.

In this Letter, we report all-electron relativistic calculations of the total energies, optimized geometries, and electronic and thermodynamic properties of perfect stoichiometric UN and UN₂ single crystals using spin-polarized DFT. To the best of our knowledge, this study is a first step assessment of the accuracy of all-electron relativistic *ab initio* calculations in modelling actinides/first-row elements moieties. Theoretical analysis of the type and strength of bonding at the molecular level in uranium nitrides should shed light on the unusual electronic structure and thermodynamic stability of these systems. The methodology will be applied to transuranic nitride systems and compared with the experimental results.

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2. Computational methods

First-principles all-electron relativistic calculations of the total energies and optimized geometries were performed using the spin-polarized density functional theory (DFT) [12]. The exchange correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Wang and Perdew [13] (PW91). Double numerical basis sets including polarization functions on all atoms (DNP) were used in the calculations. The DNP basis set corresponds to a double- ζ quality basis set with d-type polarization functions added to atoms heavier than hydrogen. The DNP basis set is comparable to 6-31G** Gaussian basis sets [14] with a better accuracy for a similar basis set size [12,15]. In the generation of the numerical basis sets, a global orbital cutoff of 5.9 Å was used. The energy tolerance in the self-consistent field calculations was set to 10^{-6} Hartree. Optimized geometries were obtained using an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of 2×10^{-3} Hartree/Å. The Monkhorst-Pack special k -point scheme [16] was used with a $4 \times 4 \times 4$ mesh for structural optimizations and electronic and thermodynamic properties calculations. In order to calculate the band structure, a k -point path along the X–R–M–G–R symmetry points [17] has been used to sample the Brillouin zone (BZ). A mesh of $6 \times 6 \times 6$ k -points was used to calculate the density of states, with a Gaussian broadening of 0.002 Hartree applied.

3. Results and discussion

Uranium dinitride and mononitride have face-centered cubic crystal lattices, with CaF₂-type and NaCl-type structures, respectively (cf. Fig. 1). Both compounds belong to the hexoctahedral isometric space group $Fm\bar{3}m$. The calculated lattice parameters for the relaxed cubic unit cells are $a = 5.28$ Å for UN₂ and 4.90 Å for UN, in excellent agreement with the experimental values of $a = 5.31(1)$ Å [18] and 4.8880(1) Å [19], respectively. Recently, the lattice parameter of a pure UN₂ sample was measured by X-ray diffraction (XRD) to be 5.30266(3) Å [20]. Calculated interatomic distances between uranium and nitrogen shells are given in Table 1. Calculations show very good agreement with our recent extended X-ray absorption fine structure (EXAFS) and XRD spectroscopic measurements [20,21]. The smallest distance between uranium atoms in UN crystal, $d_{U_0-U_1} = 3.46$ Å, is close to the 3.4 Å limit given by Hill [22] for the onset of magnetism in actinide systems. The total energies of the relaxed UN and UN₂ single crystals are -119060.2725 Hartree and -119279.7185 Hartree, respectively.

Figs. 2 and 3 display the band structures and the corresponding densities of states (DOS) of UN₂ and UN. The valence band near the Fermi level (E_F) of UN₂ is dominated by N 2p-orbital contributions while U 6d and U 5f characters play only a smaller role. Some degree of p–f hybridization appears at the top of the valence band. f-

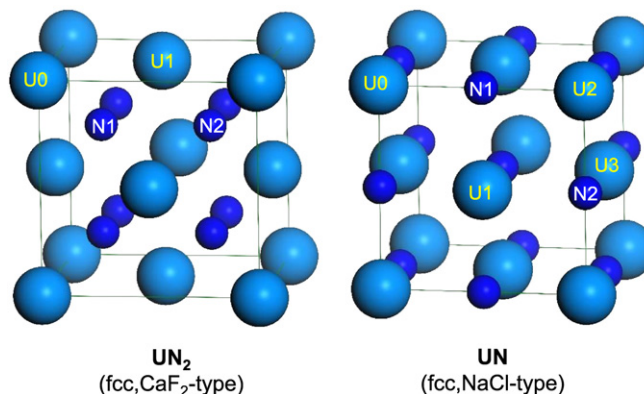


Fig. 1. Crystal structures of UN₂ and UN.

Table 1
Interatomic bond lengths in UN₂ and UN crystals (XRD and EXAFS data are from Refs. [20,21])

Crystal	Bond	R (Å)		
		This work	EXAFS	XRD
UN	U0–N1	2.45	2.43	2.44
	U0–U1	3.46	3.45	3.45
	U0–U2	4.90	4.88	4.88
	U0–N2	5.48	5.56	5.45
	U0–U3	6.00	5.94	5.97
UN ₂	U0–N1	2.28	2.28	2.299
	U0–U1	3.73	3.73	3.754
	U0–N2	4.38	4.38	4.402
	U0–U2	5.28	5.27(5)	5.30266(3)

Orbitals contribute prominently to the conduction peaks, separated from the Fermi level by a 0.90 eV indirect band gap. As a result of the contraction of the lattice parameter from the UN₂ to the UN phase, U 6d- and U 5f-orbitals overlap more efficiently in the UN phase and a large degree of d–f hybridization is observed in the valence band near the Fermi level, while the N 2p-orbital contribution tends to vanish. The conduction band is still strongly marked by f-orbitals with some degree of hybridization with d orbitals. Due to the large overlap of d and f-orbitals near the Fermi energy, the UN phase exhibits a clear metallic behavior. The calculated electron density of states at the Fermi surface is 18.1 states/eV for UN, close to the experimental estimate of ~ 20 states/eV [23].

Fig. 4 shows the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the UN₂ and UN structures. Consistent with the DOS shown in Fig. 2, the HOMO of UN₂ shows 2p π -bonding character between the N atoms while the HOMO of UN is characterized by 6d–5f hybridization between U atoms. The LUMO of both UN₂ and UN structures is dominated by 5f-orbitals connecting U atoms.

The vibrational frequencies of the normal modes of UN and UN₂ crystals have also been calculated at 0 K using finite differences of the analytic gradient of energy with respect to atomic positions. All atoms were used to evalu-

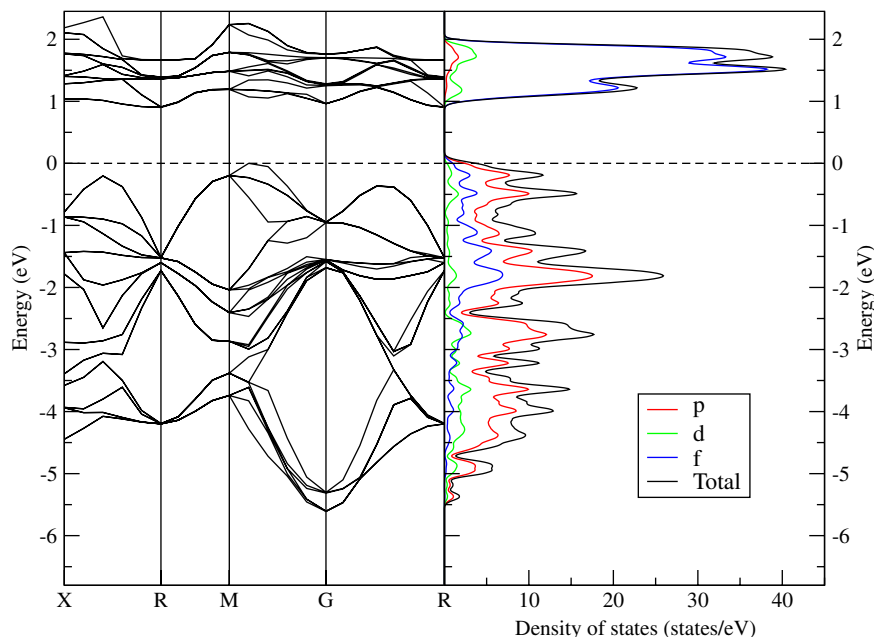


Fig. 2. Band structure and total and projected density of states of UN₂. The Fermi energy is set to zero.

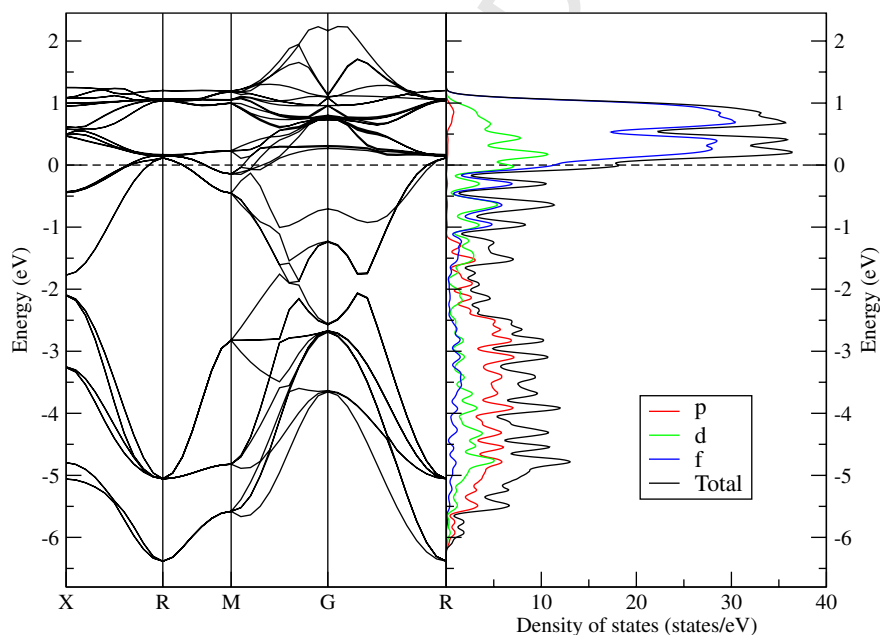


Fig. 3. Band structure and total and projected density of states of UN. The Fermi energy is set to zero.

ate Hessian matrix elements. Frequencies are reported in
 Table 2. Using these values, the lattice contribution to
 the isobaric heat capacity, C_P , has been computed as a
 function of temperature of the system, T , using the relation

$$C_P^{\text{vib}}(T) = R \sum_i \frac{(h\nu_i/k_B T)^2 \exp(-h\nu_i/k_B T)}{[1 - \exp(-h\nu_i/k_B T)]^2}, \quad (1)$$

where R is the gas constant, k_B the Boltzmann's constant, h
 the Planck's constant and ν_i is the individual vibrational
 frequencies. Calculated lattice contributions to the isobaric

heat capacities of UN and UN₂ are displayed in Fig. 5,
 along with the experimental data of Counsell et al. [1]
 and Oetting and Leitnaker [24] for UN. The calculated heat
 capacity of UN is in very good agreement with experiments
 up to 200 K, while it systematically underestimates experi-
 mental values at higher temperatures. In addition to the
 lattice vibration, the contribution associated with the con-
 duction electrons to the heat capacity has to be taken into
 account. The electronic heat capacity of a free-electron
 Fermi gas is given by [25]

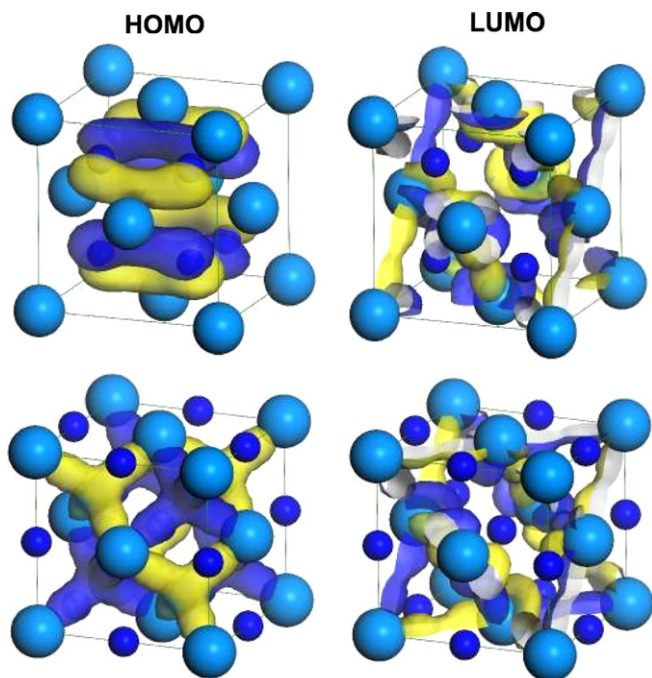


Fig. 4. Highest occupied (left) and lowest unoccupied molecular orbitals (right) of UN₂ (top) and UN (bottom) single crystals.

$$C_p^{\text{el}}(T) = \frac{\pi^2}{3} k_B^2 N(E_F) T = \gamma T, \quad (2)$$

where $N(E_F)$ is the electronic density of states at the Fermi level. The calculated value $N(E_F) = 18.1$ states/eV (cf. Fig. 3) corresponds to a coefficient $\gamma = 42.6$ mJ K⁻² mol⁻¹, in good agreement with the experimental value of $\gamma = 49.6$ mJ K⁻² mol⁻¹ [26]. This value of γ is significantly larger than the value of 3.1 mJ K⁻² mol⁻¹ for ThN [27], an

Table 2
Frequencies of the normal modes of UN₂ and UN single crystals (in cm⁻¹)

$\nu(\text{UN}_2)$	$\nu(\text{UN})$
143.31(3)	141.31(6)
143.32(3)	164.06(3)
221.30(3)	323.90(3)
284.90(6)	324.02(3)
316.70(3)	358.75(3)
395.53(3)	371.39(3)
559.53(6)	
572.93(3)	
646.29(2)	
646.35(1)	

The degeneracy of the modes is given between parenthesis.

isostructural analog of UN with unfilled 5f-shells (Th: [Rn]6d²7s², U: [Rn]5f³6d¹7s²). This provides further evidence of the important role played by itinerant 5f-electrons in thermodynamic and electronic properties of uranium mononitride. The UN isobaric heat capacity including electronic corrections is displayed in Fig. 5. Calculations reproduce calorimetric data of Counsell et al. [1] and Oetting and Leitnaker [24] within 4%. The linear dependence of the heat capacity with temperature due to conduction electrons is clearly seen above 500 K, as the lattice contribution tends to a constant value.

4. Conclusion

All-electron relativistic calculations using the spin-polarized density functional theory have been performed to model perfect stoichiometric UN and UN₂ single crystals. Structural properties measured in recent extended X-ray absorption fine structure and X-ray diffraction experiments

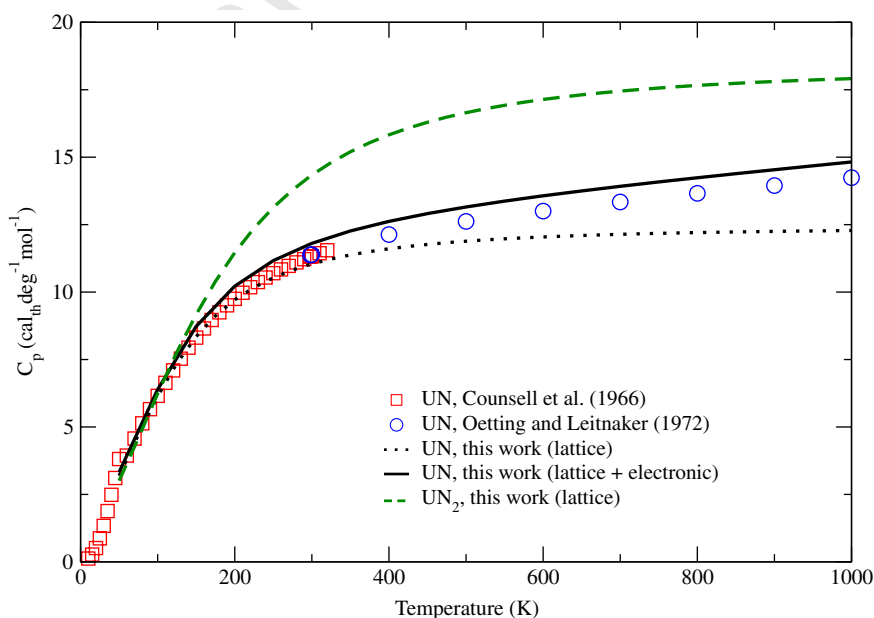


Fig. 5. Heat capacity of UN and UN₂. Experimental data of Counsell et al. [1] and Oetting and Leitnaker [24] for UN are also displayed (1 cal_{th} = 4.184 J).

are successfully reproduced within 0.03 Å error at this level of theory. Calculated densities of states and molecular orbitals show the importance of d–f hybridization and p-orbital contributions in the valence band of UN and UN₂, respectively, while f-orbital character dominates the conduction band of both compounds. The calculated isobaric heat capacity of UN, including both lattice and conduction electron contributions, agrees with calorimetric measurements to within 4% error. These results constitute a first step in assessing the accuracy of all-electron relativistic *ab initio* calculations in modelling actinides/first-row elements moieties. Further calculations will be carried out with other first-row elements, which have the capacity to bridge between actinide centers, as well as transuranic elements with first-row elements. Understanding the nature of such bonds is vital to the development of actinide chemistry [6].

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