

Point defects in thorium nitride: A first-principles study



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ABSTRACT

Thorium and its compounds (carbides and nitrides) are being investigated as possible materials to be used as nuclear fuels for Generation-IV reactors. As a first step in the research of these materials under irradiation, we study the formation energies and stability of point defects in thorium nitride by means of first-principles calculations within the framework of density functional theory. We focus on vacancies, interstitials, Frenkel pairs and Schottky defects. We found that N and Th vacancies have almost the same formation energy and that the most energetically favorable defects of all studied in this work are N interstitials. These kind of results for ThN, to the best authors' knowledge, have not been obtained previously, neither experimentally, nor theoretically.

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1. Introduction

Thorium carbides and nitrides are considered as potential nuclear fuels for Generation-IV reactors [1]. The main reason for this are the many physical advantages that these compounds present when compared to the oxide ones. Thorium carbides and nitrides have higher melting points, lower thermal expansion coefficients, larger thermal conductivities and better neutronic properties than oxide fuels.

One of the most important issues to be treated is their response under irradiation [2]. This is essential for a clear understanding of the thermophysical and structural properties under the extreme conditions provided by irradiation. A first step in the evaluation of these processes is the study of point defects, as irradiation is a relevant source for the appearance of different kinds of defects. The study of point defects is also important as they can function as trapping centers for other species.

We have recently reported on studies of point defects in ThC [3]. In the literature, there are few first-principles studies on ThN and to our best knowledge, nothing has been reported on point defects in this compound, neither theoretically, nor experimentally. Lu et al. [4] calculated lattice parameters, electronic structure, mechanical and thermodynamic properties of ThN. Atta-Fynn and Ray [5]

investigated the structural, electronic and magnetic properties. Shein et al. [6] obtained structural parameters, densities of states and spectra of K-edge X-ray emission and absorption. Modak and Verma [7,8] obtained the electronic structure, phonon dispersion relations, elastic constants, structural phase transitions, and pressure-volume equations of state under pressure (0–100 GPa).

We are going to compare, here, *ab initio* obtained results for point defects in ThN with results available in the literature for other nitride compounds with the same NaCl-type structure. For example, Kotomin et al. [9–11] reported calculated formation and migration energies of point defects and the inclusion of O impurities in UN, while Tsetseris et al. [12] studied structure, stability and interaction energies for defects in TiN, HfN and ZrN.

Summarizing, in this work, we report on, *ab initio* obtained, structural parameters, formation energies, charge densities and densities of states for several point defects (vacancies, interstitials, Frenkel pairs and Schottky) in thorium nitride.

2. Calculation details

The electronic calculations are done within the framework of density functional theory (DFT) employing the Quantum ESPRESSO package [13]. The Generalized Gradient Approximation in the Perdew-Burke-Erzenhof (GGA-PBE) formulation [14] is used for the exchange and correlation potential. This approximation was already used in thorium compounds with very good results [3,4,7,15–18], also in Th [19] and in UC [20], a carbide compound

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with a similar structure. The pseudopotential used for nitrogen is a projector Augmented-Wave one selected from the Quantum ESPRESSO pseudopotential library [21]. In the case of thorium, a norm-conserving Troullier-Martins [22] pseudopotential is generated with the *atomic* software of the Quantum ESPRESSO package following Ref. [19]. We have checked that energy convergence is already attained for a cutoff of 250 Ry. The Brillouin zone is sampled with a $4 \times 4 \times 4$ k-point mesh using the Monkhorst-Pack [23] (MP) scheme for a 64-atom supercell, this mesh is enough to obtain converged results as it has already been checked for other thorium compounds [3,16,17]. The Brillouin zone integrations are carried out with the Methfessel-Paxton [24] scheme and a smearing of 0.02 Ry. The atomic positions are fully relaxed until forces are less than 0.026 eV/Å while the supercell is held fixed. We have assumed a non magnetic ground state as it has been verified by Atta-Fynn and Ray [5] by means of first-principles calculations and as it was also experimentally reported in Ref. [25].

3. Point defect formation energies

We first calculate the formation energy of Th and N single vacancies, followed by the formation energy of interstitial defects in a tetrahedral position or forming a dumbbell. The considered dumbbells are along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. We also calculate the energy for the formation of Frenkel pairs, that are built by a vacancy and an interstitial of the same species. If the two constituting defects of a Frenkel pair are far from one another in such a way that they do not interact, we are in the presence of an isolated Frenkel pair. On the contrary, if these two defects are in neighboring positions the Frenkel pair is said to be bound. Finally, we calculate the formation energies of Schottky defects. These defects are formed by one Th and one N vacancies. As in the case of the Frenkel defects, we consider unbound and bound Schottky defects. The formation energies are obtained using the following expressions after Ref. [26],

a) Vacancy formation energy

$$E_f^{VX} = E^{N-1} - E^N + E_X, \quad (1)$$

where E^N is the energy of the 64 atoms supercell without defects, E^{N-1} is the energy of the supercell with a vacancy and E_X is the energy per atom in which X stands for a Th or a N atom. We calculate this reference energy for Th as the energy per atom in its fundamental FCC structure and for N as the energy per atom in the N_2 molecule.

b) Interstitial formation energy (tetrahedral position or dumbbell):

$$E_f^{IX} = E^{N+1} - E^N - E_X, \quad (2)$$

where E^{N+1} is the energy of the supercell with the interstitial.

c) Bound Frenkel pair formation energy

$$E_f^{FX} = E_{FX}^N - E^N, \quad (3)$$

where E_{FX}^N is the energy of the supercell with the bound Frenkel pair.

d) Isolated Frenkel pair energy is obtained from the sum of energies calculated with expressions 1 and 2

$$E_f^{iFX} = E_f^{VX} + E_f^{IX}. \quad (4)$$

e) Schottky formation energy

$$E_f^{SCH} = E^{N-2} - E^N + E_N + E_{Th} \quad (5)$$

where E^N is the energy of the 64 atoms supercell without defects, E^{N-2} is the energy of the supercell with a N and a Th vacancies.

4. Results and discussion

In the following we discuss the calculated structural parameters and the electronic properties followed by results on Th and N single vacancies. Then Th and N interstitials are presented. Finally, Frenkel pairs and Schottky defects are analyzed.

4.1. Structural parameters and electronic properties

ThN has a NaCl-type (B1) structure, which has only two atoms in its primitive cell. Fitting the total energy (Fig. 1) with a fourth order Birch-Murnaghan equation of state [27] we obtain the equilibrium lattice parameter a_0 , the bulk modulus, B_0 , and its derivative, B'_0 . We compare our results with experimental data [28,29] and with previous theoretical ones [4,5,7,30] (see Table 1); which also use GGA-PBE for the exchange and correlation potential. The equilibrium lattice parameter, as well as B_0 and B'_0 show a very good agreement with experiments and with previous calculations.

The evolution of the lattice parameter under pressure is calculated using the Murnaghan equation of state [27]. In Fig. 2 we plot these values (black line) normalized with the equilibrium lattice parameter, this ratio is called the relative lattice parameter. We compare with those obtained through a structural relaxation using the Broyden-Fletcher-Goldfarb-Shanno method (open circles) and with experimental data from Ref. [28] (full black circles). For pressures below 20 GPa the calculated relative lattice parameter shows an excellent agreement with the experimental one, while for larger pressures the observed difference is less than 1%; which gives confidence to the selected pseudopotentials.

In Fig. 3 we show the density of states (DOS) at equilibrium volume of ThN without defects. It agrees well with previous calculations [4,7].

In the inset of Fig. 3, the contour plot of the charge density in the (100) plane for defect free ThN is presented.

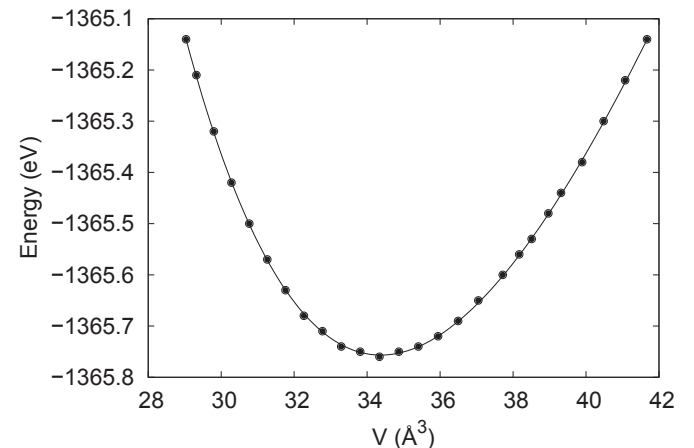


Fig. 1. Total energy as a function of volume, fitted with a fourth order Birch-Murnaghan equation of state at 0 K for ThN.

Table 1

Lattice parameter a_0 , bulk modulus B_0 and its derivative B'_0 , comparison between experimental and theoretical results.

	a_0 (Å)	B_0 (GPa)	B'_0
This work	5.161	179.17	4.19
Exp.	5.167 [28], 5.16 [29]	175 [28]	4.0 [28]
Shein et al. [30]	5.181	179.63	4.15
Lu et al. [4]	5.18	176.1	3.9
Modak et al. [7]	5.177	180.8	4.49
Atta-Fynn et al. [5]	5.181	178	–

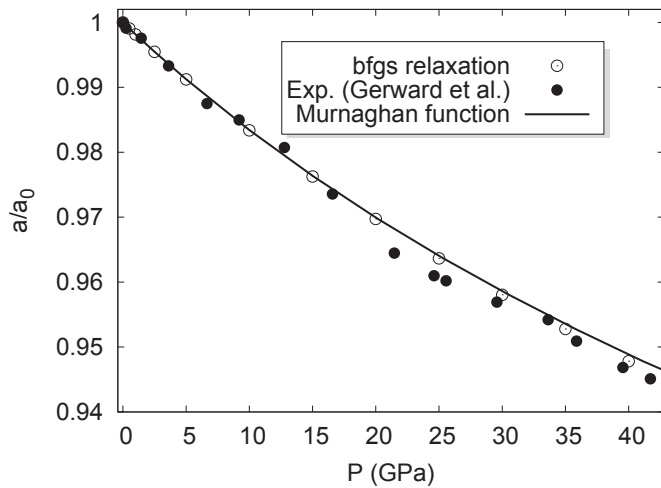


Fig. 2. Relative lattice parameter as a function of pressure for ThN at $T = 0$ K. We compare the experimental data [28] (full black circles) with the values obtained with a Broyden-Fletcher-Goldfarb-Shanno structural relaxation (bfgs) (open circles) and with the values calculated with the Murnaghan equation of state using the parameters of Table 1 (black line).

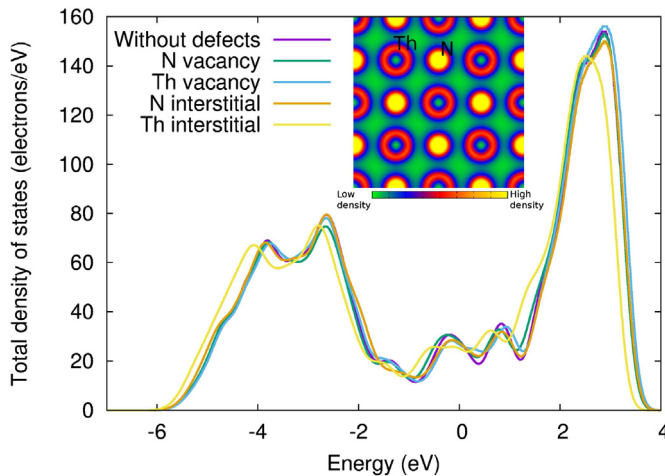


Fig. 3. Calculated total density of states of ThN for a super-lattice without defects (violet solid line) containing 64 atoms and with N (green solid line), Th (light blue solid line) vacancies and Th (orange solid line) and N (yellow solid line) tetrahedral interstitials. (Inset) Charge density contour plot in the (100) plane for ThN without defects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The charge density is almost symmetrically distributed around Th and N. This suggests the presence of an ionic character with a certain degree of covalency, which explains its metallicity. A Bader [31] analysis of the charge density gives a charge transfer of 1.73e from thorium to nitrogen.

4.2. Vacancies

In Table 2 the results obtained for the vacancies' formation energies of ThN are shown. Nitrogen and thorium vacancies have almost the same formation energy. The N vacancy's formation energy is slightly smaller than the thorium one. A similar behavior is observed in UN, whose structure is also of the NaCl-type. The formation energies of nitrogen and uranium vacancies are also similar in the last compound, being the one corresponding to the nitrogen vacancy also the smaller one [10]. This contrasts with what is obtained for carbon compounds, such as UC [26] and ThC [3]. In these carbon compounds a carbon vacancy is energetically much more favorable than the uranium or thorium ones.

In the presence of vacancies the neighboring atoms to the defects undergo relaxations as it can be seen in Table 2, for the present case. The nitrogen vacancy induces an outwards displacement, of 0.04 Å, of the six thorium atoms first nearest neighbors of the vacancy. The six N atoms nearest neighbors of the thorium vacancy relax 0.16 Å outwards. This kind of outwards relaxation is also observed in UN [9], UC [26] and ZrC [32]. Otherwise, the Th or N vacancies induce almost no displacements of the second-nearest-neighbors and the lattice is nearly not disturbed as a whole.

In Fig 3 we show the DOS of ThN for a lattice with Th and N vacancies. We note that there is almost no difference with the DOS for a lattice without defects, as expected, due to the small fraction of defects and the localized nature of the perturbation induced in the lattice.

In Fig. 4 (a) the charge density of ThN in the (100) plane containing a N vacancy is shown. Nearly no lattice distortion occurs due to this defect, as already mentioned. Through a charge density Bader analysis we observe that the six thorium atoms first-nearest-neighbors of the N vacancy increase their charge in 0.24e. The same behavior was observed in UN [9]. In Fig. 4 (b) the (100) plane charge density of ThN in the presence of a Th vacancy is shown. The Th vacancy induces an increased covalency among the surrounding N-Th bonds. The six nitrogen first nearest neighbors see their charge almost not modified.

4.3. Interstitials

We focus in this section on another common defect in irradiated materials: self-interstitials. The formation energies for these defects are calculated for a tetrahedral position and in the dumbbell configuration for thorium and nitrogen atoms.

Interstitial formation energies as a function of a N interstitial position in the ThN lattice are shown in Fig. 5. We note that the lowest formation energy corresponds to a nitrogen in a tetrahedral position (0.4 eV) followed by the <110> (1.66 eV) and the <111> (1.70 eV) dumbbells. The formation energy for the interstitial tetrahedral position is smaller than the one corresponding to a nitrogen vacancy. Tsetseris et al. reported a similar behavior for HfN [12]. On the contrary, in ThC [3] and UC [26] the dumbbell configurations of carbon are more energetically favorable than the tetrahedral interstitial one.

The binding distances are almost the same for the tetrahedral position as for the <111> dumbbell (see Fig. 6 (c)) for nitrogen

Table 2

Vacancy formation energy (E_f^{VX}) for thorium and nitrogen in the ThN structure and atomic displacements (δR) of first (1nn) and second (2nn) nearest-neighbors of the vacancy.

Vacancy	E_f^{VX} (eV)	δR 1nn (Å)	δR 2nn (Å)
Thorium	3.97	0.16	-0.04
Nitrogen	3.69	0.04	0

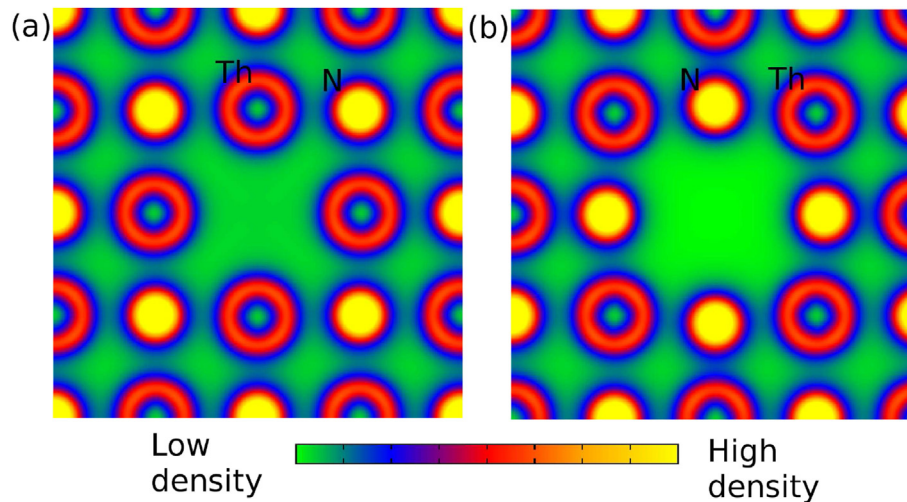


Fig. 4. Charge density contour plot in the (100) plane for ThN. (a) With a N vacancy. (b) With a Th vacancy.

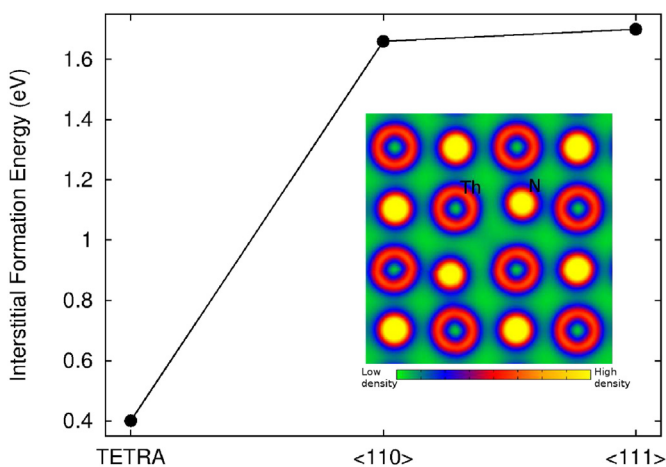


Fig. 5. Interstitial formation energies as a function of three N interstitial positions in the ThN lattice: tetrahedral and dumbbells in $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. (Inset) Charge density contour plot in the (100) plane in the atomic layer right above the N tetrahedral interstitial defect for ThN.

interstitials (see Table 3). In the $\langle 110 \rangle$ dumbbell case the binding distance is shorter, as in this orientation the two nitrogen atoms are allowed to get closer (see Fig. 6 (a)). The N-Th distance, between the N tetrahedral interstitial and a first thorium neighbor is 2.44 \AA , that is smaller than the 2.58 \AA distance between a thorium and a nitrogen in the defect free lattice. The N tetrahedral interstitials produce an outwards displacement of 0.30 \AA of the four nearest N atoms, as it is possible to observe in the inset of Fig. 5. The four nearest Th atoms also move 0.01 \AA outwards.

The Th interstitial formation energy as a function of interstitial position in the ThN lattice is shown in Fig. 7. We observe that the lowest formation energy corresponds to a tetrahedral interstitial (8.54 eV), followed by the $\langle 111 \rangle$ (9.48 eV) and the $\langle 110 \rangle$ (11.36 eV) dumbbell configurations. We have observed the same behavior for ThC [3].

Throughout the Bader charge analysis we observe a charge transfer of $1.22e$ from a thorium atom in a tetrahedral position to the neighboring nitrogen atoms, while that of a thorium atom in a $\langle 111 \rangle$ dumbbell is of $1.10e$ and in a $\langle 110 \rangle$ dumbbell it is of $1.06e$. In the case of Thorium in the perfect lattice the charge transfer is of

$1.73e$. The charge density contour plots of these three interstitials are shown in the inset of Figs. 5 and 6 (b) and Fig. 6 (d).

The binding distances of the thorium dumbbells and the distance to the first Th or N neighbor in the case of tetrahedral interstitials are almost the same for the Th-Th bond in the tetrahedral position as for the two dumbbell orientations. The N-Th distance, between the thorium in the tetrahedral interstitial and a first nitrogen neighbor is 2.38 \AA , that is smaller than the 2.58 \AA distance between a thorium and a nitrogen in the lattice without defects. The tetrahedral interstitial produces an outwards displacement of 0.12 \AA of the four nearest Th atoms, while the four nearest N atoms move 0.46 \AA outwards (see Fig. 7 (Inset)).

4.4. Frenkel pairs and Schottky defects

Finally, we obtain the formation energies of isolated and bound Frenkel pairs and of Schottky defects. Bound Schottky defects are calculated for the two directions $\langle 100 \rangle$ and $\langle 111 \rangle$. For bound Frenkel pairs the interstitial atom is in a tetrahedral position within the contiguous cube containing the vacancy. To obtain the Th formation energy of isolated Frenkel pairs, we add the formation energy of a tetrahedral interstitial and of a single vacancy individually calculated in different supercells (see Equation (4)).

In the case of thorium Frenkel pairs, there is an effective attractive interaction between the vacancy and the interstitial defect, due to this the energy difference between the bound and the isolated Frenkel pairs is -0.32 eV (see Table 4).

The charge transfer of Th in a Frenkel pair is $1.28e$, while the charge transfer of a Th interstitial (single defect) is $1.22e$. Therefore, the charges of the surrounding atoms are also very similar in both cases. The same is observed for the surroundings of bound and isolated Th vacancies.

In the case of nitrogen Frenkel pairs, a strong effective repulsion between vacancy and interstitial defects appears, as there is a big positive energy difference of 4.0 eV between them (see Table 4).

In Table 5 we show the formation energies for Schottky defects. We observe an effective repulsion interaction between vacancies along the $\langle 100 \rangle$ direction (positive energy difference, 0.41 eV) and a very small effective attractive interaction along the $\langle 111 \rangle$ direction (negative energy difference, -0.05 eV). This behavior is similar to the one obtained for Schottky defects in ThC, which presents an energy difference of 1.2 eV between isolated and $\langle 100 \rangle$ Schottky

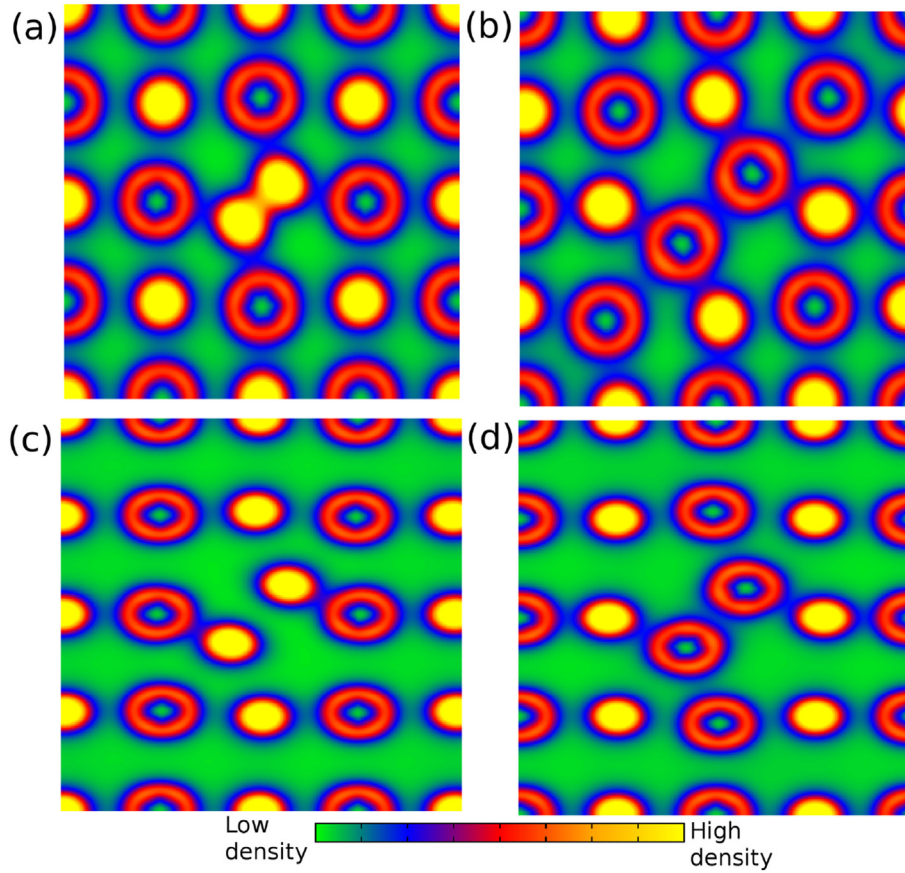


Fig. 6. Charge density contour plots of ThN. (a) Nitrogen dumbbell in <110> direction. (b) Thorium dumbbell in <110> direction. (c) Nitrogen dumbbell in the <111> direction. (d) Thorium dumbbell in the <111> direction.

Table 3
Binding distances of the dumbbells and distance to first-nearest-neighbor Th or N of tetrahedral interstitials (in Å).

Interstitial	Dum<111>	Dum<110>	Tetra	Tetra
Thorium	2.68	2.60	2.80 (Th-Th)	2.38 (Th-N)
Nitrogen	2.62	1.40	2.60 (N-N)	2.44 (Th-N)

Table 4
Formation energy (E_f^{VX}) for thorium and nitrogen isolated and bound Frenkel pairs. The interstitial atom of the Frenkel pair is in a tetrahedral position. In the case of the bound Frenkel pairs the interstitial is in the contiguous cube to the one containing the vacancy.

	Thorium	Nitrogen
FP bound (eV)	15.18	8.09
FP isolated (eV)	15.51	4.09

Table 5
Formation energy for thorium and nitrogen isolated and bound (in <100> and <111> directions) Schottky defects.

	<100>	Isolated	<111>
Schottky (eV)	7.25	7.66	7.71

defects and -0.07 eV between isolated and <111> ones [3]. The Bader charges of atoms surrounding vacancies in the <111> direction are almost the same as those appearing in the isolated defect, as expected. The charge transferred by each Th, neighbor of a N vacancy in the Schottky defect along the <100> direction, is $1.62e$ while in the case of an isolated N vacancy it is $1.49e$.

5. Conclusions

We have calculated structural parameters, electronic properties and formation energies of several point defects in ThN by means of first-principles calculations within the framework of DFT.

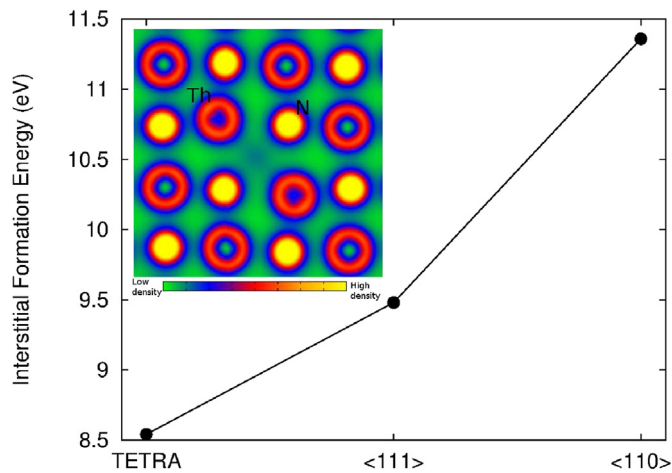


Fig. 7. Interstitial formation energies as a function of three Th interstitial position in the ThN lattice: tetrahedral and dumbbells in <111> and <110> directions. (Inset) Charge density contour plot in the (100) plane in the atomic layer right above the Th tetrahedral interstitial defect for ThN.

Formation energies for vacancies, interstitial and Frenkel pairs and Schottky defects were also obtained.

The values of the lattice constant, bulk modulus and its derivative agree very well with previous experimental and theoretical results. The same is valid for the relative lattice parameter as a function of pressure. These results are in good agreement with experimental data.

We found that N and Th vacancies have almost the same formation energies, a similar behavior is reported by Kotomin *et al.* for UN [10]. On the contrary, in ThC [3] and UC [26] it was found that carbon vacancies are energetically more favorable than thorium or uranium ones.

In the case of nitrogen interstitial defects, the tetrahedral position is energetically most favorable. This also occurs in HfN, but not in ThC [3] and UC [26] where the dumbbell configurations are preferable. For nitrogen interstitials the tetrahedral position is the energetically most favorable, too. It happens differently in UC and ThC. We also found that the N tetrahedral interstitial is most energetically favorable than the N vacancy as it was also shown by Tsetseris *et al.* for HfN [12]. The energetically most favorable defects of all treated defects in this work are the ones corresponding to N interstitials.

Finally, we analyzed Frenkel pairs and Schottky formation energies, and observed that for Th Frenkel pairs there is an effective attractive interaction between vacancy and interstitial. On the contrary, there is a strong effective repulsion between vacancy and interstitial for nitrogen Frenkel pairs. For Schottky defects an effective repulsion between vacancies in the $\langle 100 \rangle$ direction and a very small effective attraction in the $\langle 111 \rangle$ direction are found. We have already reported the same behavior for ThC [3].

Considering the lack of experimental and theoretical data on point defects in ThN we hope that this work encourages new research on this topic.

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