



Original Article

Computational study of protactinium incorporation effects in Th and Th compounds

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ABSTRACT

Protactinium contamination is a mayor issue in the thorium fuel cycle. We investigate, in this work, the consequences of Pa incorporation in vacancy defects and interstitials in Th, ThC and ThN. We calculate charge transfers and lattice distortions due to these incorporations as well as migration paths and energies involved in the diffusion of Pa.

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1. Introduction

In the search after better nuclear fuels for Generation-IV reactors [1] there has been a boost in the research work on thorium and its compounds (ThC and ThN) [2–11]. They have higher melting points, lower thermal expansion coefficients and larger thermal conductivities than their uranium counterparts [12].

In the Thorium fuel cycle, ^{232}Th , the fertile material, captures a neutron forming ^{233}Th . This becomes ^{233}Pa through.

β^- decay, which develops into the fissile ^{233}U , also by β^- decay [13]. ^{233}Pa has a 27 days long half-life that enables the possibility of a neutron capture resulting in a decline of the ^{233}U production [14,15]. This is the so-called protactinium effect.

Experimentally, Lorentz et al. determined the solubility of Pa in Th [16], while Schmitz et al. obtained the corresponding diffusion coefficient of Pa in Th [17].

On the simulation side, within the framework of Density functional theory (DFT), N. Richard et al. [18] investigated the crystal

structure of Thorium and J. Bouchet et al. [19] studied its high-pressure lattice dynamics and thermodynamic properties. In previous works, we have studied the stability and formation energies of vacancies, interstitials, and divacancies in Thorium and the effect of incorporation of Xe, He, Kr [4] and oxygen [7] atoms in Th defects and also self-diffusion.

Regarding ThN, Y. Lu et al. [20], P. Modak and A. K. Verma [21] and R. Atta-Fyn and A. K. Ray [22] obtained electronic, mechanical and thermodynamic properties, phonon dispersion relations, elastic constants and structural phase transitions. We have obtained the formation energy of defects, such as vacancies, interstitials, Frenkel pairs and Schottky defects in Refs. [23] and oxygen incorporation in Ref. [4].

In the case of ThC, structural, mechanical, electronic and thermodynamic properties were investigated by S. Aydin et al. [24] and by I. V. Lim and G. E. Scuseria [25]. While Shein et al. obtained X-ray emission (XES) and absorption (XAS) spectra [26] and elastic properties [27] of ThC. We have calculated the phonon spectrum and thermophysical properties in Refs. [28]. We also obtained point defect formation energies for ThC [29], He, Xe, Kr and O incorporation energies [30] and self-diffusion [31].

Taking into account that the presence of Pa in the thorium fuel cycle is of technical interest and that there is a lack of information

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Table 1
Incorporation energy (eV) of a Pa atom in tetrahedral interstitials and vacancy defects in Th, ThC and ThN.

	Interstitial (eV)	Vacancy (eV)	
Th	5.19	− 1.59	
ThC	2.88	−6.26 (Th)	5.82 (C)
ThN	7.63	−4.00 (Th)	6.31 (N)

on this subject in the literature, we study in this work the effect of having Pa atoms in Th, ThC and ThN lattices by means of DFT calculations. This is done by obtaining the energy of incorporation of Pa in vacancy and interstitial sites. Lattice distortions and charge transfers due to Pa incorporation are also analyzed. Finally, energy and migration paths are calculated.

2. Calculation and numerical details

Thorium's crystal structure is a face centered cubic with an experimental equilibrium lattice parameter, \AA , of 5.085 \AA [32]. In our previous work we obtained for a_0 , 5.045 \AA [4]. Thorium carbide and thorium nitride have both a NaCl-type (B1) structure and experimental equilibrium lattice parameters of 5.335–5.344 \AA [33] and 5.167 \AA [34], respectively. For these compounds we previously obtained 5.335 \AA (ThC) [28] and 5.161 \AA (ThN) [23]. The global charge of the analyzed systems is neutral.

The expressions used to calculate the incorporation energies are those of Ref. [35]. The incorporation energy of a protactinium atom in a tetrahedral interstitial position is given by

$$E_{Pa}^{lint} = E^{N+1} - E^N - E_{Pa}, \quad (1)$$

where E^N is the energy of a supercell without defects and E^{N+1} is the energy of a supercell with a Pa atom incorporated in a tetrahedral interstitial position and E_{Pa} is the energy per protactinium atom in the ground state. The incorporation energy in a vacancy site is given by

$$E_{Pa}^{Ivac} = E^{N-1} - E_{Pa}^N - E_{Pa}, \quad (2)$$

where E^{N-1} is the energy of the supercell with a vacancy, E_{Pa}^N is the energy with a Pa atom in a vacancy site.

We also calculate the solution energy, E^{sol} , as the energy required to create the defect and the subsequent incorporation of an atom into that defect. It is defined as

$$E^{Sol} = E^I + E^F, \quad (3)$$

where E^I is the incorporation energy (in a vacancy or in an interstitial position) and E^F is the defect formation energy. In the case of incorporation in an interstitial position the solution and the incorporation energies are the same.

We obtain the charge transfer to protactinium atoms incorporated in interstitial and vacancy sites by doing a Bader analysis [36].

The behavior of Pa atoms in these materials is analyzed through the calculation of migration energies along different paths. This is done using the nudged elastic band (NEB) method [37]. The minimum energy path from an initial to a final state is obtained by optimizing a set of intermediate images of the system. From these paths we obtain the migration energies.

First-principle calculations are done with the software package Quantum ESPRESSO [38] based on the density functional theory. The reliability of the calculations made with this software in these systems has already been proven in several works, see Refs. [4,28]. The Generalized Gradient Approximation in the

Table 2
Solution energy (eV) of a Pa atom incorporated in tetrahedral interstitials and vacancy defects in Th, ThC and ThN.

	Interstitial (eV)	Vacancy (eV)	
Th	5.19	0.51	
ThC	2.88	−0.42 (Th)	5.97 (C)
ThN	7.63	−0.03 (Th)	10.0 (N)

Perdew–Burke–Erzenhof (GGA–PBE) formulation [39] is used for the exchange and correlation potential. Thorium and protactinium pseudopotentials are norm-conserving Troullier–Martins [40] ones and are generated with the *atomic* software available in the same package following Ref. [18]. The pseudopotentials for carbon [41] and nitrogen [42] are taken from the Quantum ESPRESSO pseudopotential library. In these calculations, 64 atoms supercells in the cases of ThC and ThN and a 32 atoms supercell in the case of Th, are used. These supercell sizes are large enough to avoid spurious interactions due to the periodicity. For energy convergence a 250 Ry cutoff is considered. To sample the Brillouin zone, we use a Monkhorst–Pack [43] (MP) scheme together with a $4 \times 4 \times 4$ k-point mesh. The integrations are performed with the Methfessel–Paxton [44] scheme and with an energy smearing of 0.02 Ry. The atomic positions are fully relaxed till forces are less than 0.026 eV/ \AA . The migration paths and energies are obtained with the NEB method as implemented in the Quantum ESPRESSO software package [38].

3. Results and discussions

3.1. Incorporation and solution energies

Incorporation energies of protactinium in tetrahedral interstitial positions and in Th, C and N vacancies of the systems under study are shown in Table 1. It is worth mentioning that incorporation energies, as defined in Eqs. (1) and (2), do not take into account composition deviations and thermal effects, but, despite this fact they can be well considered as a first step in the analysis of this topic. A lower incorporation energy value implies a more favorable incorporation position and a negative energy indicates that the incorporated atom is energetically stable in the lattice.

We observe that the energetically more favorable position is a Th vacancy in the three cases. In fact, we note that in these cases the incorporation energies are negative, on the contrary the other incorporation sites present positive energies, suggesting energetically unstable positions. This is the expected behavior as thorium and protactinium have similar atomic radii.

Solution energies calculated using equation (3) are presented in Table 2. Vacancy formation energies were previously obtained in Ref. [4] for Th, in Refs. [29] for ThC and in Ref. [23] for ThN.

We notice that even taking into account the energy cost of forming a Th vacancy, the energy necessary to incorporate protactinium in the vacancy is still negative for ThC and ThN. In the case of Th, although it is not negative it is very small. The other incorporation sites, studied in this paper, are energetically very unfavorable.

3.2. Lattice distortions due to Pa atoms

The protactinium atoms in the lattices of Th, ThC and ThN produce distortions that affect the surrounding atoms. Pa atoms incorporated in thorium vacancies give rise to inward displacements of the neighboring atoms for Th (0.03 \AA), ThC (0.13 \AA), and ThN (0.11 \AA), as expected due to the similar atomic radii of Pa and Th. Large outward displacements of the four first nearest neighbor

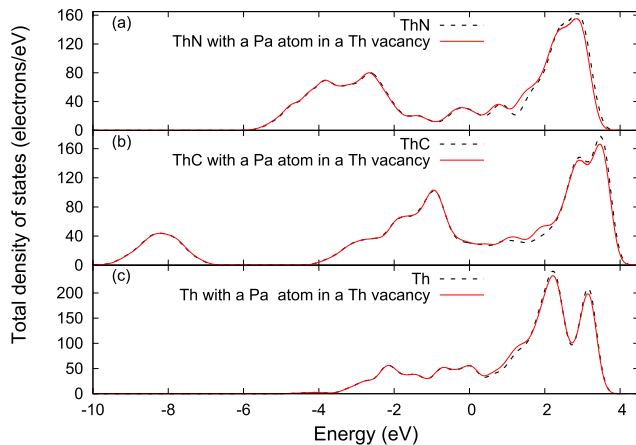


Fig. 1. Total density of states as a function of energy for a lattice without defects and a lattice with a Pa atom incorporated in a Th vacancy site in (a) Thorium nitride. (b) Thorium carbide. (c) Thorium.

Th atoms occur when Pa is in a tetrahedral interstitial site, 0.47 Å in Th, 0.38 Å in ThC and 0.44 Å in ThN. This behavior is similar to the one taking place when incorporating a thorium atom in interstitial sites in Th [4], ThC [29], and ThN [23]. If a Pa atom is incorporated in a C vacancy, it yields an outward displacement of 0.20 Å of the six nearest thorium atoms. In the case of a N vacancy there is a 0.16 Å outward displacement of the neighboring thorium atoms.

3.3. Electronic structure

In Fig. 1 we show total densities of states (DOSs) as a function of energy for the three systems under study. In panel (a) we compare the DOSs of ThN without defects and with a Pa atom incorporated in a Th vacancy. In panel (b) and (c) we plot the same but for ThC and Th, respectively.

We observe that the difference between the DOSs with and without an incorporated Pa atom lies just above the Fermi energy. In the three cases the difference between the DOSs with defect and without defect is very small, this might be related to the low concentration of Pa in the lattice. It is worth mentioning that oxygen with the same low concentration makes an appreciable difference in the DOSs, as we already observed in Ref. [7]. Therefore, the small difference can also be attributed to the similarity between Th and Pa.

3.4. Charge transfer

The charge transferred to protactinium atoms in interstitial positions and in vacancy defects are obtained through a Bader charge [36] analysis (see Table 3).

Just for comparison, we mention that in the case of pure ThC the charge transfer from Th to C is $-1.81e$ [29] and in the case of ThN the charge transfer from Th to N is $-1.72e$ [23]. When introducing Pa the largest transfer takes place when it is incorporated in a Th vacancy, which coincides with the energetically most favorable

Table 3

Charge transferred to an incorporated Pa atom in interstitial positions and in vacancy defects obtained through Bader analysis for Th, ThC and ThN.

	Interstitial	Vacancy	
Th	$-0.45e$	$-0.30e$	
ThC	$+1.11e$	$+1.89e$ (Th)	$-0.14e$ (C)
ThN	$+1.20e$	$+1.85e$ (Th)	$-0.53e$ (N)

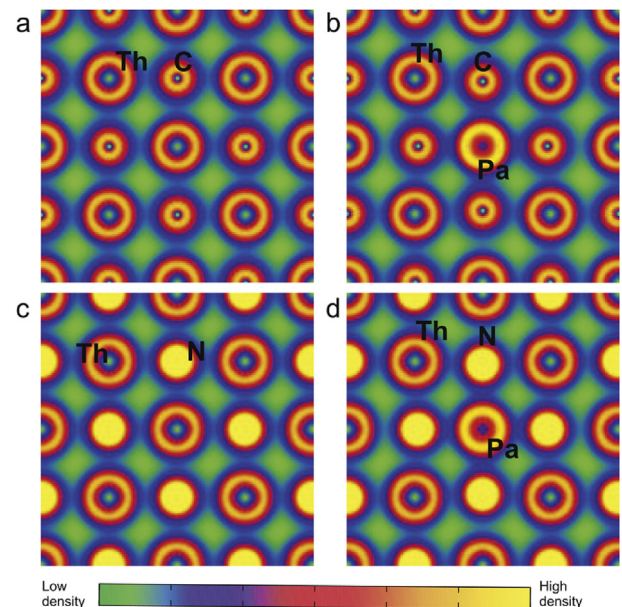


Fig. 2. Charge density contour plots. (a) ThC without defects. (b) Pa atom in a Th vacancy in ThC. (c) ThN without defects. (d) Pa atom in a Th vacancy in ThN.

incorporation site. It is also similar to the charge transferred to C and N in ThC and ThN, respectively. For Pa incorporated in an interstitial position, in the case of Th, the charge transfer is larger than in the vacancy case.

In Fig. 2 we show charge density contour plots. We note that a Pa atom in a Th vacancy presents a larger covalent bonding to its nearest C (Fig. 2 (b)) or N (Fig. 2 (d)) neighbor than Th (Fig. 2 (a) and (c)). This is evident from the fact that the electronic charge density is larger in these cases than for Th. This should show up also when comparing the values of the vacancy formation energies for Th in ThC and in ThN and, the incorporation energies of Pa in the same compounds. This is precisely what happens, in the case of ThC the vacancy formation energy and the incorporation energy are 5.84 eV and 6.26 eV respectively, while for ThN the energies are 3.97 eV and 4.00 eV. This is similar to the behavior of the cohesive energy of '3d', '4d' and '5d' transition metals, which increases with increasing 'd' occupation, if the occupations correspond to less than half filling. In our case, responsible for the value of the incorporation energy, as well as for the relative degree of covalency, is the filling of the '5f' band. Both Th and Pa have a less than half filled '5f' level, and Pa has one '5f' electron more than Th. Thereafter it is reasonable that Pa presents a stronger covalent bond to its 'sp' neighbors than Th.

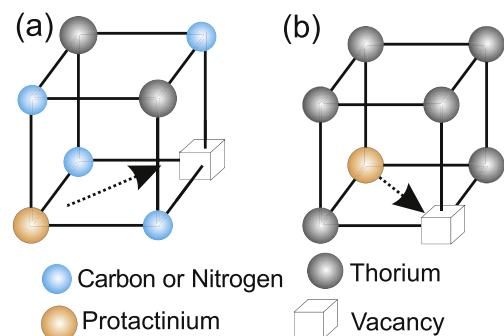


Fig. 3. Pa migration path through Th vacancy sites. (a) ThN or ThC with NaCl type structure. (b) Thorium FCC.

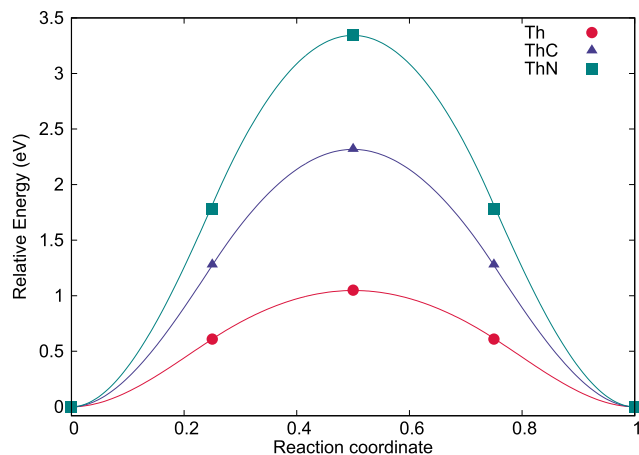


Fig. 4. Relative energy (eV) as a function of the reaction coordinate for the migration of a Pa atom through a Th-vacancy path in Th (red circles), ThC (blue triangles), and ThN (green squares). The energies are relative to the initial configurations. The lines are an interpolation of the path energy profile that goes exactly through each image. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4

Migration energy (eV) for a Pa atom through a Th-vacancy path for Th, ThC and ThN.

Th	ThC	ThN
1.05	2.32	3.35

3.5. Migration of Pa atoms

When analyzing the diffusion of protactinium through the lattices of Th, ThC, and ThN, we only calculate migration through thorium vacancy paths (see Fig. 3), as incorporation of protactinium in Th vacancies is energetically more favorable than in C and ones.

In Fig. 4 we present the energy barriers for a protactinium atom migrating from one vacancy to another. We observe that the highest energy barrier is obtained for ThN. In Table 4 the migration energies for these paths are shown. This indicates that the Pa atoms should migrate more easily in ThC than in ThN and in Th than in ThC.

The same behavior is observed for the migration of an O atom through these materials [7].

4. Conclusions

We studied some consequences of the presence of Pa atoms in Th and in its compounds by means of density functional theory calculations.

The incorporation and solution energies of Pa in interstitial and vacancy sites in Th and compounds were calculated. Incorporation of Pa in Th vacancies was found to be energetically more favorable than incorporation in interstitial sites.

Atomic displacements, electronic structures and charge transfers were also analyzed. It was observed that there is almost no change in the DOS when a Th atom is replaced by a Pa one.

NEB calculations were performed and migration paths and energies for Pa atoms through Th vacancies were calculated for Th and its compounds. It was found that the migration energy is lowest in the case of pure Th and highest in the case of ThN.

We conclude that Pa atoms, that substitute Th atoms, will migrate through Th-vacancy paths and that the Th compound with the smaller migration energy is ThC.

We hope this work encourages more experiments and new

calculations on these systems due to the technical interest of this subject.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2020.03.017>.

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