



A first-principles study of He, Xe, Kr and O incorporation in thorium carbide



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ABSTRACT

Thorium-based materials are currently being investigated in relation with their potential utilization in Generation-IV reactors as nuclear fuels. Understanding the incorporation of fission products and oxygen is very important to predict the behavior of nuclear fuels. A first approach to this goal is the study of the incorporation energies and stability of these elements in the material. By means of first-principles calculations within the framework of density functional theory, we calculate the incorporation energies of He, Xe, Kr and O atoms in Th and C vacancy sites, in tetrahedral interstitials and in Schottky defects along the (111) and (100) directions. We also analyze atomic displacements, volume modifications and Bader charges. This kind of results for ThC, to the best authors' knowledge, have not been obtained previously, neither experimentally, nor theoretically. This should deal as a starting point towards the study of the complex behavior of fission products in irradiated ThC.

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1. Introduction

Thorium and its compounds (carbides and nitrides) [1,2] are being investigated as possible materials to be used as nuclear fuels for Generation-IV reactors [3]. These compounds present several physical advantages as compared to uranium ones. In particular, thorium carbides and nitrides have higher melting points, lower thermal expansion coefficients and larger thermal conductivities than their uranium counterparts.

In recent years there have been several first-principles studies, for example, Modak and Verma studied the electronic properties, phonon dispersion relations, elastic constants and structural phase transitions of ThN within Density Functional Theory (DFT) using pseudopotentials [4]. Lu et al. investigated the electronic structure, mechanical and thermodynamic properties derived from, *ab initio* obtained, lattice dynamics data on the same compound [5]. Using an all-electron approach and local orbitals, Atta-Fyn and Ray obtained the structural, electronic and magnetic properties of ThN [6].

In the case of ThC, Lim and Scuseria obtained their structural parameters and electronic properties using gaussian-type-orbitals within DFT and comparing the results coming from the use of

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several types of functionals [7]. Structural, mechanical, electronic and thermodynamic properties of ThC also were investigated by Aydin et al. doing pseudopotential calculations for different exchange and correlation potential within and beyond the usual local density approximation [8]. Shein et al. calculated structural parameters, electronic properties, X-ray emission (XES) and absorption (XAS) spectra [9] and elastic properties [10] of ThC. In our previous works on ThC, we obtained the phonon spectrum, the mechanical and thermophysical properties [11] and we reported on the energetics of several point defects [12].

Actually, during the fission processes many fission products and α particles are produced and, thereafter, one of the most important issues to be studied is the behavior of these materials under irradiation [13]. Fission products can induce bubble formation, which is at the origin of swelling and degradation of thermal conductivity across the fuel-clad gap. Therefore, understanding the consequences of the incorporation of fission products and He atoms is important for the prediction of the behavior of nuclear fuels.

A first approach to this goal is the estimation of incorporation energies by means of state of the art simulations. In the case of uranium, Klipfel et al. investigated the incorporation of volatile elements (xenon, krypton, cesium and iodine) in UN [14]. Bévilion et al. studied the incorporation and stability of several fission products in UC [15] while Freyss analyzed the presence of helium and xenon impurities in UC [16]. These data for ThC and ThN, to the best authors' knowledge, have not been yet obtained.

In this work, we report and analyze the results obtained for the incorporation energies of He, Xe, Kr and O atoms in ThC by means of *ab initio* calculations. As stated above, due to α decays, He atoms are also present in nuclear fuels along with the other products. The incorporation of He is important due to its effects during long-term storage. In the fission processes one of the most abundant products is xenon, which together with krypton and helium have a key role in bubbles' formation. On the other hand, oxygen can be incorporated due to its strong affinity with carbide fuels.

We calculate the incorporation energies of He, Xe, Kr and O atoms in vacancy sites of Th and C, in tetrahedral interstitial positions and in Schottky defects along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions. We obtain and analyze atomic displacements, volume modifications and Bader charges. This should deal as a starting point towards the study of the complex behavior of fission products in irradiated ThC.

2. Calculation details

The electronic calculations are done within the framework of Density Functional Theory (DFT) employing the Quantum ESPRESSO package [17]. The Generalized Gradient Approximation in the Perdew–Burke–Erzenhof (GGA–PBE) formulation [18] is used for the exchange and correlation potential. This functional approximation has already been proven to give accurate results in the case of ThC [11,12,8]. Even if DFT–GGA does not take into account van der Waals interactions, which are of relevance in the calculation of binding properties of noble-gases, it was reported to describe correctly the incorporation of helium in Fe [19], helium and xenon in UC [16] and xenon and krypton in UN [14]. The pseudopotential used for carbon is an ultrasoft one from the Quantum ESPRESSO pseudopotential library [20]. In the case of thorium, a norm-conserving Troullier–Martins [21] pseudopotential is generated with the *atomic* software of the same package following Ref. [22]. A 250 Ry energy cutoff is used. The pseudopotentials for helium, xenon, krypton and oxygen are norm-conserving ones also from the Quantum ESPRESSO pseudopotential library [23]. The Brillouin zone is sampled by a $6 \times 6 \times 6$ k-point mesh using the Monkhorst–Pack [24] (MP) scheme for a 64 atoms supercell. We have checked the energy convergence as a function of energy cutoff and k-points' number. The Brillouin zone integrations are carried out with the Methfessel–Paxton [25] scheme and with an energy smearing of 0.02 Ry. The atomic positions are fully relaxed till forces are less than 0.026 eV/Å. For volume optimization a 0.01 GPa threshold is used.

ThC is a metal [7] whose structure is of the NaCl-type (B1). The experimental equilibrium lattice parameter, a_0 , is 5.335–5.344 Å [2]. In our previous work [11], using the same pseudopotentials, we obtained $a_0 = 5.335$ Å.

There are different possibilities for the incorporation of fission products in the ThC lattice, we consider their incorporation in C or Th vacancy sites, in tetrahedral interstitial positions and in existing Schottky defects along the $\langle 111 \rangle$ or $\langle 100 \rangle$ directions. The formation energy of Schottky defects, which are very important in the incorporation of helium and fission products, has not been calculated previously for ThC.

The formation and incorporation energies are obtained using the following expressions after Ref. [16],

(a) Schottky formation energy.

$$E_{for}^{Sch} = E^{N-2} - E^N + E_C + E_{Th}, \quad (1)$$

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

E_C and E_{Th} are the energies per atom of carbon and thorium, respectively, in their ground states.

(b) Incorporation energy of an atom of type X in a vacancy site.

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

where E^{N-1} is the energy of the supercell with a C or Th vacancy, E_X^N is the energy of the system with a He, Xe, Kr or O atom incorporated in the vacancy and E_X is the energy of the isolated incorporated atom (He, Kr, Xe) or one half the energy of an isolated oxygen molecule.

(c) Incorporation energy in a tetrahedral interstitial.

$$E_X^{int} = E_X^{N+1} - E^N - E_X, \quad (3)$$

where E_X^{N+1} is the energy of the supercell with the incorporated atom in a tetrahedral interstitial position.

(d) Incorporation energies in a Schottky defect

$$E_X^{sch} = E_X^{N-1} - E_{for}^{Sch} - E_X, \quad (4)$$

where E_X^{N-1} is the energy of the supercell with an atom incorporated in the Schottky defect, E_{for}^{Sch} is the energy of the supercell with a Schottky defect along the $\langle 111 \rangle$ or $\langle 100 \rangle$ directions.

As reference energies, E_X , we choose for Th and C the energy of the corresponding element in its pure bulk state and for the incorporated impurities the energy of the isolated atoms or atoms in a molecule, as it is usually done. We compare the outgoing energies with results available for other compounds with the same NaCl-type structure in the literature [16,26]. The reference energy for thorium is the energy per atom in its fundamental FCC structure, for carbon it is the energy per atom in the graphite structure. The energy per atom of an isolated O₂ molecule is used as reference for oxygen and, for He, Xe and Kr the energy of isolated atoms is used.

3. Results and discussions

In the following, we first discuss results obtained for formation energies of Schottky defects along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, followed by the discussion of the incorporation energies. Then, we analyze the atomic displacements and volume modifications due to the presence of the incorporated atoms. Finally, the results of the Bader analysis are presented.

3.1. Formation energies

The Schottky defects are formed by one Th and one C vacancies. If the two constituting vacancies of a Schottky defect are far enough from each other, so that they do not interact, we are in the presence of an unbound Schottky defect. On the contrary, if these two vacancies are in neighboring positions the Schottky defect is said to be bound. This defect type is a major candidate for incorporation of fission products, oxygen impurities and helium atoms due to its abundance.

The formation energy of a bound Schottky defect along the $\langle 111 \rangle$ is 6.06 eV and along the $\langle 100 \rangle$ direction it is 4.79 eV. In the case of an unbound Schottky defect, the formation energy is 5.99 eV. We obtain this last value by adding the formation energies of a C vacancy (0.15 eV) and a Th vacancy (5.84 eV), calculated in a previous work [12] within the same calculation approach. The difference in energy between bound and unbound Schottky defects in the $\langle 111 \rangle$ direction is 0.07 eV and -1.2 eV in the $\langle 100 \rangle$. This shows that vacancies at second-nearest-neighbor positions (along $\langle 111 \rangle$ direction) almost do not interact. We also observe that there is an effective attractive interaction between Th and C vacancies. This behavior is similar to the one found by Freyss [16] for UC.

3.2. Incorporation energies

The incorporation energies as defined in Eqs. (2)–(4) do not take into account neither composition deviation nor thermal effects [27,28]. Despite this fact and just as a first step of analysis following Ref. [14,16,26,29], it can be said that a lower energy indicates a more favorable incorporation site. We also remark that a negative energy implies that the incorporated atom is energetically stable in the lattice. In Table 1, we show the incorporation energies for five different sites (Th and C vacancy sites, tetrahedral interstitials and Schottky defects along $\langle 111 \rangle$ and $\langle 100 \rangle$).

For He, Xe and Kr the most favorable incorporation site is the thorium vacancy in the $\langle 100 \rangle$ Schottky defect, followed by the isolated thorium vacancy and the thorium vacancy site in a Schottky defect along the $\langle 111 \rangle$ direction. These last two sites present almost the same formation energies. The most favorable sites are coincident with the larger size of the incorporation sites (Th vacancy defects and Th vacancies in Schottky defects). The most unfavorable site is the tetrahedral interstitial. The formation energies in the case of He in Th vacancies and He in Schottky defects are small enough to favor the solubility of He in ThC. On the contrary, in the case of Xe and Kr the large formation energy values would favor bubbles' formation. In Fig. 1 incorporation energies as a function of atomic radius of He, Xe and Kr are shown. We notice that the smaller the atomic radius the smaller the incorporation energy for the five types of defects. From Fig. 1 it is clear that for the three incorporated atoms the sequence of incorporation energies is the same $\langle 100 \rangle$ Schottky is the most stable and interstitial tetrahedral positions are the less stable ones.

In the case of oxygen impurities, the most favorable incorporation site is the C vacancy, with almost no difference with the $\langle 111 \rangle$ Schottky defect with the oxygen atom in the C vacancy site, as expected. The formation energies are negative indicating the stability of the incorporation of oxygen in ThC. In this case the most disfavored incorporation site is the Th vacancy. The behaviors found are comparable to those obtained in UC [16].

3.3. Atomic displacements and volume modifications

In Table 2, we present the atomic displacements, after relaxation, of the first nearest-neighbors of the incorporated atoms. For an atom incorporated in a C (Th) vacancy there are six Th (C) first nearest-neighbors, for a tetrahedral interstitial, there are four Th and four C first nearest-neighbors. All resulting displacements are positive indicating outward movements. Helium incorporated in a Th vacancy does not induce an additional relaxation to the one already induced by the vacancy (a Th vacancy produces an outward displacement of 0.29 Å, see Ref. [12]) which indicates that the relaxation is mainly due to the missing thorium. Both, Xe and Kr incorporations produce greater outward displacements of their first nearest-neighbors than the original vacancies, consistent with their larger atomic radii. Oxygen incorporation in a C vacancy site drives the C neighbors to return to the original positions in the ThC undistorted lattice, being this defect the energetically most stable for oxygen impurities.

Table 1
Incorporation energies (eV) for He, Xe, Kr and O in ThC at five different of incorporation sites (Th and C vacancies, tetrahedral interstitial and Schottky defects along $\langle 111 \rangle$ and $\langle 100 \rangle$).

	Vac C	Vac Th	Tetra int	Sch(100)	Sch(111)
He	1.24	0.41	2.00	0.32	0.40
Kr	3.68	1.98	8.38	1.28	2.05
Xe	4.99	2.33	10.55	1.55	2.40
O	-6.45	0.25	-3.49	-5.87	-6.52

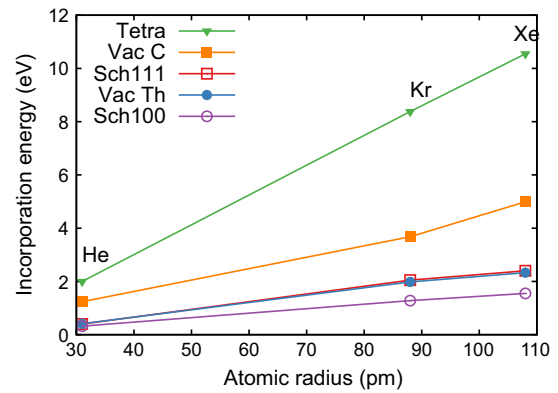


Fig. 1. Incorporation energy as a function of atomic radius for He, Xe and Kr atoms incorporated in different defects in ThC.

Table 2

Atomic displacements of the first nearest-neighbors (nn) of the defects (in Å). For a C (Th) vacancy there are six Th (C) nn, for a tetrahedral interstitial there are four Th and four C nns.

	Vac C (Th)	Vac Th (C)	Tetra int
He	0.17	0.29	0.07 (Th)/0.10 (C)
Kr	0.25	0.37	0.31 (Th)/0.29 (C)
Xe	0.29	0.36	0.40 (Th)/0.32 (C)
O	0.03	0.37	0.00 (Th)/0.28 (C)

As a first approach to estimate the possible swelling of the thorium carbide crystal in the presence of diluted helium, xenon and krypton atoms we calculate the volume modifications of the supercell. In an improved analysis would have to consider the difference between the behavior of a single rare-gas atom incorporated in a single defect and the behavior of a gas bubble in a fuel matrix where the gas is under pressure. We think that these present results are a first step towards a multiscale approach to this issue.

We minimize the internal pressure of the supercell for the atoms incorporated in C and Th vacancy sites and in a tetrahedral interstitial. In Table 3 we show the absolute volume modifications ΔV (a.u.³) of the supercells and the modifications relative to the unit cell volumes V_0 , $\Delta V/V_0$ (%).

As expected, helium induces the smallest volume modification among the elements considered in this work. In the case of He in a Th vacancy the volume decreases 13%. This is due to the big difference in atomic radius between helium and thorium. A similar result was obtained by Freyss et al. in Ref. [30] for He replacing the actinide element in UO₂, PuO₂ and AmO₂. Krypton and xenon both induce large volume modifications (larger swelling) than helium. Even in the case of a Th vacancy we obtain positive volume variations. For all three elements, the bigger is the volume modification, the larger is the incorporation energy.

Table 3

Modification of the volume due to the incorporation of He, Xe and Kr. ΔV (a.u.³) absolute supercell volume modification and $\Delta V/V_0$ (%) volume variations relative to the unit cell of ThC, V_0 .

	Vac C		Vac Th		Tetra int	
	ΔV	$\Delta V/V_0$ (%)	ΔV	$\Delta V/V_0$ (%)	ΔV	$\Delta V/V_0$ (%)
He	26	10	-33	-13	41	16
Kr	130	51	30	12	252	98
Xe	187	73	44	17	325	127

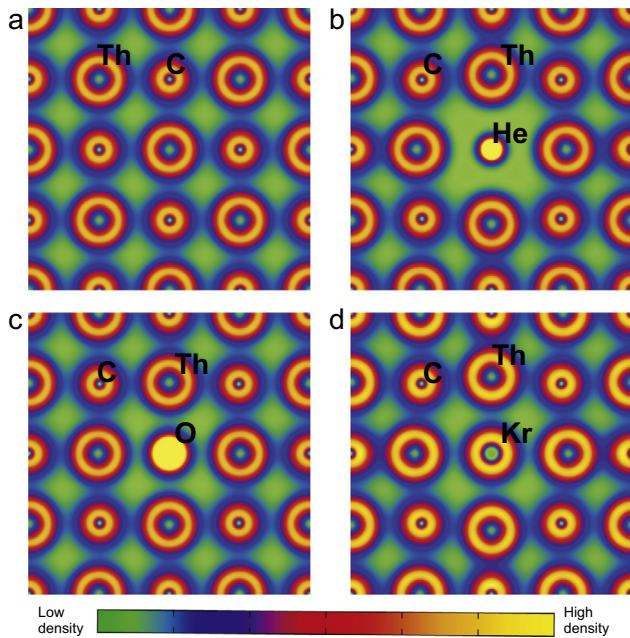


Fig. 2. Charge density contours plot in the (100) plane for (a) ThC without defects, (b) ThC with a He atom incorporated in a C vacancy, (c) ThC with an O atom incorporated in a C vacancy, (d) ThC with a Kr atom incorporated in a C vacancy.

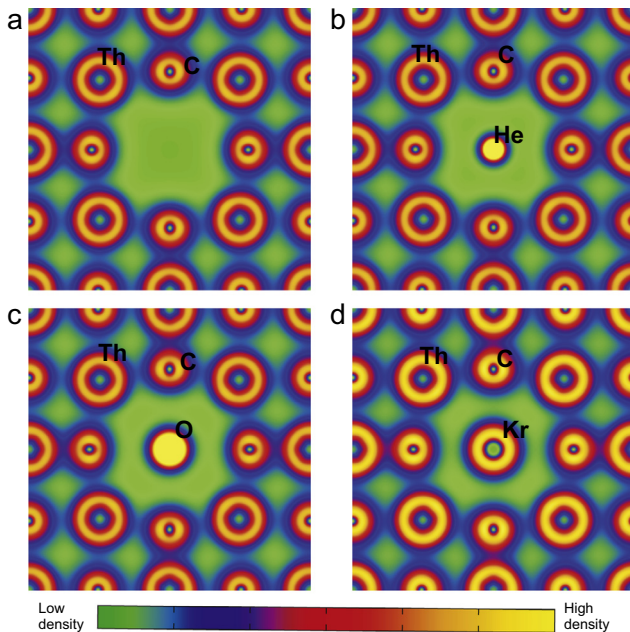


Fig. 3. Charge density contours plot in the (100) plane for (a) ThC with a Th vacancy, (b) ThC with a He atom incorporated in a Th vacancy, (c) ThC with an O atom incorporated in a Th vacancy, (d) ThC with a Kr atom incorporated in a Th vacancy.

Table 4
Bader analysis of the charge density of ThC after the incorporation of He, Xe, Kr and O in a C vacancy, in a Th vacancy and in a tetrahedral interstitial.

	Vac C	Vac Th	Tetra int
He	−0.10	−0.07	−0.1
Kr	−0.34	−0.11	−0.23
Xe	−0.38	−0.01	−0.13
O	−1.41	−0.87	−1.30

3.4. Charge density and Bader analysis

In Fig. 2 and 3 we show charge density contours plots in the (100) plane for ThC without defects and with He, Kr or O atoms incorporated in C or Th vacancy sites.

In Fig. 2(c) we observe that, as stated above, the oxygen impurity incorporated in a C vacancy site restores the surrounding atoms to their positions in the perfect ThC lattice (see Fig. 2(a)). In Fig. 2(b) and (d) we note that He and Kr incorporated in a C vacancy induce lattice distortions and an increased bonding between first-nearest-neighbors thorium and carbon atoms. These effects are larger than the ones induced by the C vacancy itself.

In Fig. 3(b) we notice that the lattice distortion and increased bonding among the surrounding atoms in the ThC lattice after the incorporation of a He atom in the C vacancy, is almost the same as in the ThC lattice with only the C vacancy present. In Fig. 3(c) and (d) we observe that the lattice distortion due to the incorporation of O and Kr is almost the same as before but the bonding is stronger in the case of the Kr atom.

The results of a Bader [31] analysis of the charge density in ThC with the incorporation of He, Xe, Kr and O in different sites are shown in Table 4. For He there is a very small charge transfer, regardless of the incorporation site. For Kr and Xe the charge transfer is larger in the case of a C vacancy incorporated site, almost $-0.40e$. In the case of an oxygen impurity, there is a large charge transfer due to its electronegativity. The largest charge transfer corresponds to the incorporation of an O atom in a C vacancy ($-1.41e$), which is the energetically more favorable incorporation site. This behavior is similar to the one reported in the literature for UC [16] and UN [29].

4. Conclusions

In summary, we have performed a systematic study of incorporation energies of helium, xenon, krypton and oxygen atoms in thorium carbide. As incorporation sites we have considered C and Th vacancies, tetrahedral interstitial sites and Schottky defects (along $\langle 111 \rangle$ and $\langle 100 \rangle$ directions). We have also calculated the formation energies of Schottky defects. We have calculated and analyzed incorporation energies, atomic displacements, volume modification and Bader charges in ThC with the incorporation of some fission products. These results were obtained by means of first-principles calculations within the framework of DFT.

Using just incorporation energies analysis, we have found that for He, Xe and Kr the energetically more favorable site is the Schottky defect along $\langle 100 \rangle$, followed by the Schottky defect along $\langle 111 \rangle$ with almost the same energy as the Th vacancy. Finally, the larger incorporation energies, correspond to the C vacancy and the tetrahedral interstitial. In the case of oxygen, the more favorable site is the C vacancy followed by the Schottky defect along $\langle 111 \rangle$ direction, with almost the same energy. The incorporation energies of oxygen are mostly negative showing the stability of O in ThC and the trend towards oxidation.

Atomic displacements are found to be all in outward directions, with a maximum value of 0.37 \AA . In the case of helium in a Th vacancy the relaxation is due essentially to the missing thorium. Volume modification due to helium incorporation is at most 17%. Krypton and xenon both induce larger volume modifications (large swelling) than helium. For all three elements the larger is the volume modification, the greater is the incorporation energy.

Through a Bader analysis we have obtained that in the case of He there is a very small charge transfer, regardless the incorporation site. For Kr and Xe the charge transfer is larger for incorporation in a C vacancy, almost $-0.40e$. In the case of an oxygen impurity, there is a large charge transfer due to electronegativity

of this impurity atom. Being the C vacancy the site with largest charge transfer $-1.41e$. This behavior is similar to the one reported for UC and UN.

This work is a first step in the study of incorporation of fission products and oxygen in ThC, system for which there exists a nearly complete lack of experimental data. We hope that these results encourage to perform experiments and more calculations in these materials.

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