



First-principles study of point defects 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. One of the most important issues to be studied is their behavior under irradiation. A first approach to this goal is the study of point defects. By means of first-principles calculations within the framework of density functional theory, we study the stability and formation energies of vacancies, interstitials and Frenkel pairs in thorium carbide. We find that C isolated vacancies are the most likely defects, while C interstitials are energetically favored as compared to Th ones. These kind of results for ThC, to the best authors' knowledge, have not been obtained previously, neither experimentally, nor theoretically. For this reason, we compare with results on other compounds with the same NaCl-type structure.

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1. Introduction

As well as in the case of uranium carbides and nitrides, thorium compounds of the kind are being investigated as possible materials to be used for nuclear fuels of Generation-IV reactors [1]. In both cases the reason for the shown interest lies in 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 and larger thermal conductivities than their uranium counterparts. Irradiation being a relevant source of different kinds of defects, one of the most important issues to be studied is, precisely, the behavior under irradiation of the materials to be used or that are being used as nuclear fuels [2]. This is the case of ThC. A first approach to this goal is the study of point defects, that is essential for a clear understanding of the thermophysical and structural properties under the extreme conditions provided by irradiation.

In the literature, there are relatively few first-principles calculations dealing with the characteristics and properties of different point defects in nitrides and carbides of uranium and even less in thorium compounds.

Freyss [3] calculated the formation energies of point defects in uranium carbides and nitrides and also investigated the inclusion of impurities in UC. Ducher et al. [4] obtained the formation energies

for point defects in UC. Kotomin et al. [5–7] also reported calculated formation and migration energies of point defects and the inclusion of O impurities in UN. There are, actually, few experimental results for these uranium compounds. Vacancies' formation and migration energies have been experimentally obtained by means of resistivity measurements [9,8,10] in the case of UC. For thorium compounds, Shein and Ivanovskii [11] calculated vacancies' formation energies in the case of carbon non-stoichiometric ThC, but there are, to our best knowledge, no other results available, neither theoretical nor experimental.

In this work, we obtain by means of *ab initio* calculations the formation energies, charge densities and densities of states of several point defects (vacancies, interstitials, Frenkel pairs and anti-sites) in thorium carbide. This should deal as a starting point towards the study of the complex behavior of irradiated ThC.

2. Method of calculation

The electronic calculations are done within the framework of density functional theory (DFT) employing the Quantum ESPRESSO package [12]. The Generalized Gradient Approximation in the Perdew–Burke–Erzenhof (GGA–PBE) formulation [13] is used for the exchange and correlation potential. The pseudopotential for carbon is an ultrasoft one from the Quantum ESPRESSO pseudopotential library [14]. In the case of thorium, a norm-conserving Troullier–Martins [15] pseudopotential is generated with the *atomic* software of the Quantum ESPRESSO package following Ref. [16]. A 250 Ry cutoff is used. The Brillouin zone is sampled by a $6 \times 6 \times 6$ k-point mesh using the Monkhorst–Pack [17] (MP)

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scheme for a 64-atom supercell. The Brillouin zone integrations are carried out with the Methfessel–Paxton [18] scheme and a smearing of 0.02 Ry. The atomic positions are fully relaxed till forces are less than 0.026 eV/Å.

3. Point defect formation energies

ThC is a metal whose structure is of the NaCl-type (B1). The experimental equilibrium lattice parameter, a_0 , is 5.335–5.344 Å. [19] In our previous work [20], using the same pseudopotentials, we obtained $a_0 = 5.335$ Å.

We calculate the formation energies for Th and C vacancies and Th and C interstitial defects in a tetrahedral position or forming a dumbbell. We consider dumbbells along the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. The energy for the formation of Frenkel pairs, that are built by a vacancy and an interstitial of the same species, is also calculated. If the two constituting defects of a Frenkel pair are far enough from each other 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. We also obtain the formation energies of antisite defects, that is, for the exchange of a Th atom and its neighboring C atom.

The formation energies are calculated using the following expressions after Ref. [3],

(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 is a Th or C atom.

(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) Antisite formation energy

$$E_f^A = E_A^N - E^N, \quad (5)$$

where E_A^N is the energy of the supercell with the antisite defect.

4. Results and discussions

In the following we discuss, first, the results obtained for Th and C vacancies, followed by Th and C interstitials. Finally, the results for antisite and Frenkel pair defects are presented.

Table 1

Vacancy formation energy (E_f^{VX}) for thorium and carbon in ThC structure and atomic displacement (δR) of first (1nn) and second (2nn) nearest-neighbor of the vacancy.

Vacancy	E_f^{VX} (eV)	δR 1nn Å	δR 2nn Å
Thorium	5.84	0.29	0.03
Carbon	0.15	0.09	0.03

4.1. Vacancies

The data obtained for the vacancies' formation energies of ThC are given in Table 1. As expected, it is easier to create C vacancies than Th ones. A similar behavior is observed in UC whose structure is also of the NaCl-type, where the formation energy of an uranium vacancy is larger than the one corresponding to a carbon one [3,4]. Shein and Ivanovskii [11] reported formation energies of carbon vacancies for non-stoichiometric ThC, obtaining 0.32 eV for ThC_{0.75} and 0.49 eV for ThC_{0.50}. These data are consistent with our results for an isolated C vacancy in the stoichiometric compound. With increasing number of carbon vacancies, the C vacancy formation energy increases as it depends on the number of cut bonds.

Vacancies produce a relaxation of the neighboring atoms. We observe that a carbon vacancy induces an outward displacement of the six thorium first-nearest-neighbors of 0.09 Å. The six first-nearest-neighbors carbon atoms of the thorium vacancy relax outward by 0.29 Å. This outward relaxation is also observed in UC [3], ZrC [21] and UN [5]. Vacancies of both types of atoms produce displacements of the second-nearest-neighbors of the order of 0.03 Å.

In Fig. 1 we show the calculated total densities of states (DOS) of ThC for a lattice without defects and with Th and C vacancies. The DOS for the 64 atoms cell without defects matches well with previous calculations [23,22,24]. We note that there is almost no difference among them, as expected, due to the small fraction of defects. In Fig. 2(a) we show a contour plot of the charge density in the (100) plane for ThC without defects. The charge density is almost symmetrically distributed around Th and C atoms and there exists a weak bond along the Th–C directions. This suggests the prevalence of an ionic character. This agrees with what was stated in the previous work by Aydin et al. [22]. Lim and Scuseria [24] have also shown that the use of hybrid functionals, like the one by Heyd, Scuseria and Ernzerhof, does not modify the metallic nature of the system, properly obtained using GGA.

In Fig. 3 we show the partial local densities of states (PLDOS) on a thorium atom, first-neighbor of a carbon vacancy and for a thorium atom in a lattice without defects. We observe that the largest modification experienced by the PLDOS is an increase in the height of the peak due to the f-orbital of the thorium atom near the carbon vacancy. In Fig. 2(b) the charge density in the (100) plane of ThC with a C vacancy is shown. We note that there is almost non lattice distortion due to the carbon vacancy.

Fig. 4 shows the partial local densities of states on a carbon atom, first-neighbor of a thorium vacancy, and on a carbon atom

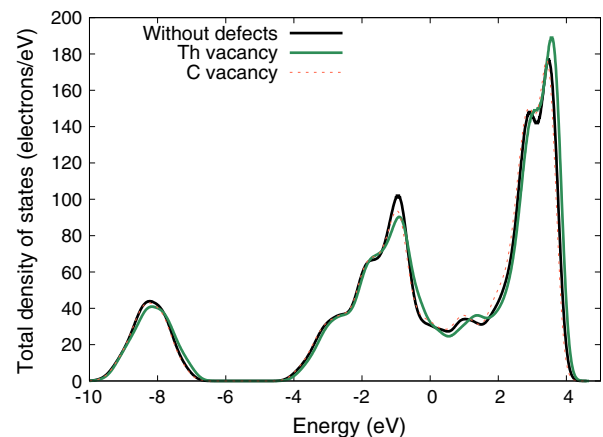


Fig. 1. Calculated total density of states of ThC for a lattice without defects (black solid line) containing 64 atoms and with Th (green solid line) and C (red dotted line) vacancies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

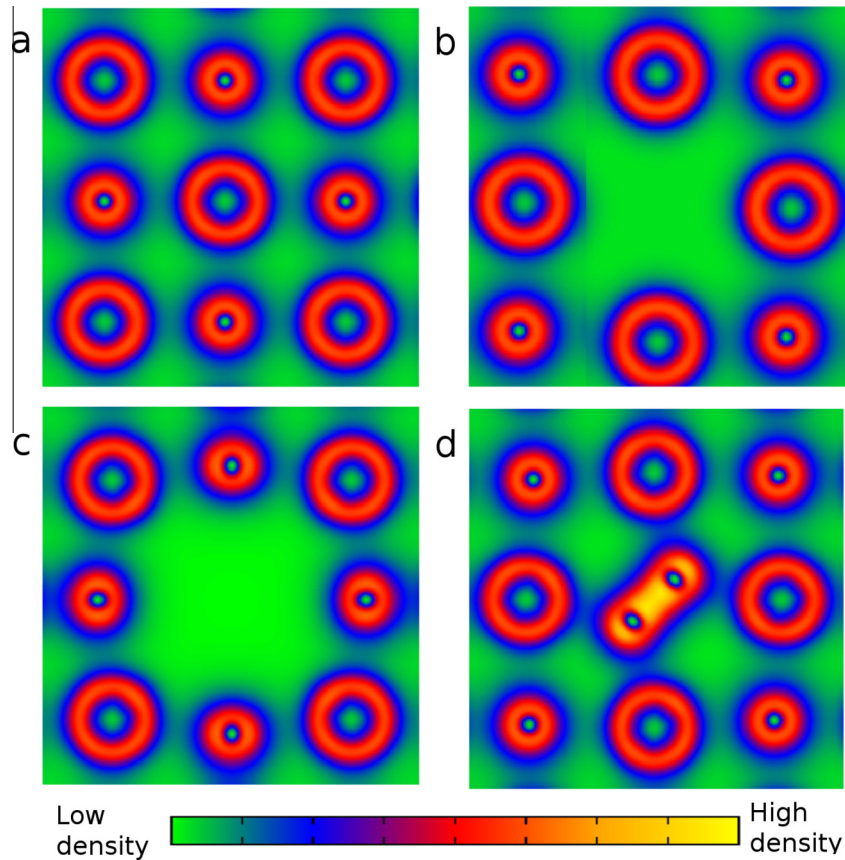


Fig. 2. Charge density contour plot in the (100) plane for (a) ThC without defects, (b) ThC with a C vacancy, (c) ThC with a Th vacancy, (d) ThC with a C (110) dumbbell in the (100) plane.

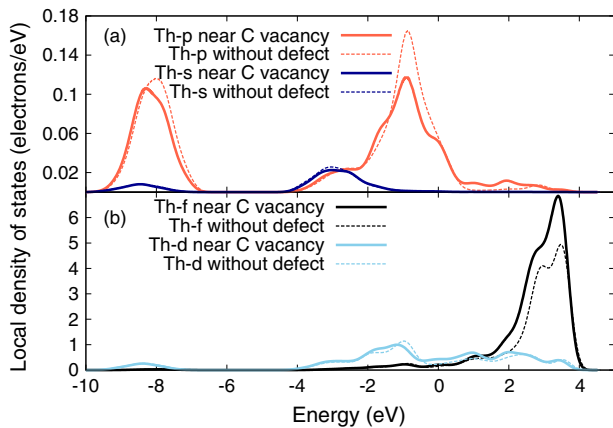


Fig. 3. PLDOSs at a thorium (solid lines) atom first-neighbor of a carbon vacancy in a 64 atoms ThC cell and for a thorium (dashed lines) atom in a lattice without defects.

within the ThC lattice without defects. We observe the splitting of the peak corresponding to the s-orbital contribution of the carbon atom near the thorium vacancy. In Fig. 2(c) we show the (100) plane charge density of ThC in the presence of a Th vacancy. We observe that the Th vacancy induces an increased covalency in the neighboring C bonds.

4.2. Interstitials

We focus in this section on another common defect in irradiated materials: self-interstitials. We calculate formation energies for

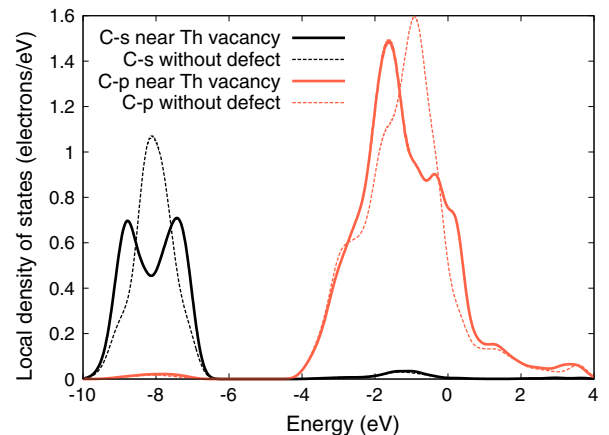


Fig. 4. Partial local densities of states for a carbon (solid lines) atom first-neighbor of a thorium vacancy and for a carbon (dashed lines) atom in a ThC lattice without defects.

these defects in a tetrahedral position and in the dumbbell configuration for thorium and carbon atoms. Dumbbells are calculated for three directions: $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$.

Interstitial formation energies as a function of C interstitial position in the ThC lattice are shown in Fig. 5. We note that the lowest energy configuration corresponds to the dumbbell in the $\langle 110 \rangle$ direction (1.11 eV), followed by $\langle 100 \rangle$ (1.18 eV), $\langle 111 \rangle$ (1.29 eV) dumbbells and finally for the tetrahedral configuration (3.52 eV). In the case of UC, the dumbbell configuration is also more stable than the tetrahedral one [3].

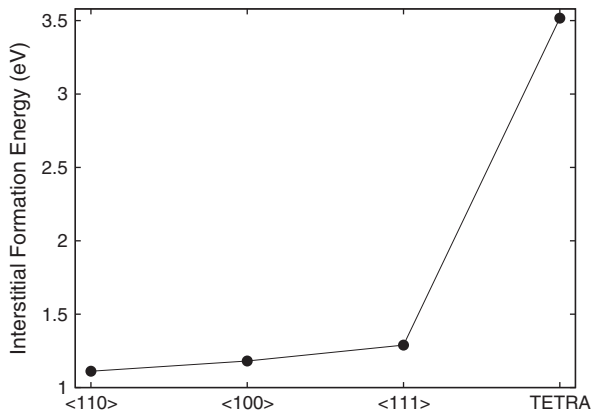


Fig. 5. Interstitial formation energies as a function of C interstitial position in the ThC lattice.

Table 2
Binding distances of the dumbbells (in Å).

Dumbbell	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$
Thorium	3.08	2.74	2.60
Carbon	1.29	1.31	1.31

In Table 2 we observe that the binding distances are almost the same for the three dumbbell directions. The tetrahedral interstitials produce an inward displacement of 0.50 Å of the four nearest C atoms and an outward displacement of 0.18 Å of the four nearest Th atoms.

For the most likely interstitial configuration, the $\langle 110 \rangle$ dumbbell, we calculate the partial local densities of states on one carbon atom in the dumbbell and compare it with those corresponding to a C atom in a lattice without defects (see Fig. 6). We note that the weight of peak (A) decreases, while it moves towards the Fermi level (see peak (B)) and peak (C) gets narrower and moves away from this energy (see peak (D)). These shifts eliminate the energy gap between peaks (A) and (C). The PLDOS of the C atom building the $\langle 110 \rangle$ dumbbell resembles the one of a C atom in a dimer (not shown). Fig. 2(d) shows the charge density in a $\langle 110 \rangle$ plane which contains a C $\langle 110 \rangle$ dumbbell, the dumbbell formation is clearly observed.

Fig. 7 presents the interstitial formation energy as a function of Th interstitial position in the ThC lattice. We observe that the

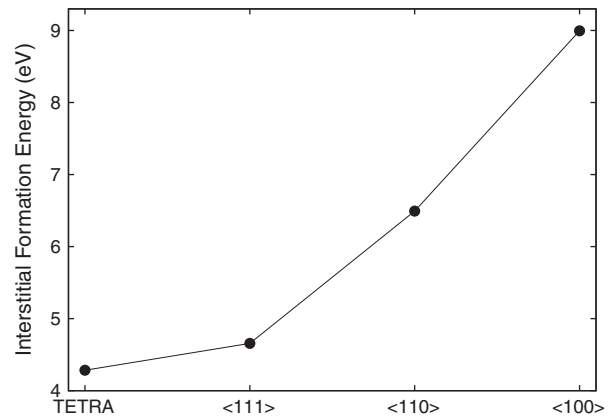


Fig. 7. Interstitial formation energies as a function of Th interstitial position in the ThC lattice.

lowest energy configuration is given for a tetrahedral interstitial (4.28 eV), followed by the $\langle 111 \rangle$ (4.66 eV), $\langle 110 \rangle$ (6.49 eV) and $\langle 100 \rangle$ (9.00 eV) dumbbells' configurations. Freyss [3] found, in UC, that the most stable configuration is the $\langle 111 \rangle$ dumbbell followed by the tetrahedral interstitial (by a difference of 0.56 eV). They also reported that the $\langle 110 \rangle$ dumbbell has a formation energy more than twice the one corresponding to the $\langle 111 \rangle$ dumbbell.

In Table 2 the binding distances for the three dumbbell directions are shown. We note that the larger the formation energy, the shorter the binding distance (bond). The tetrahedral interstitial produces an outward displacement of 0.06 Å of its four nearest C atoms and an outward displacement of 0.51 Å of its four nearest Th atoms.

We show the partial local densities of states in the case of a Th interstitial for the most likely interstitial configuration, that is the tetrahedral one, and on a Th atom in a lattice without defects (see Fig. 8). We note that the peak due to Th-f orbital grows larger, in the interstitial position, and the one corresponding to the Th-d orbital moves away from the Fermi level as compared to the defect free case.

Fig. 9 shows the total densities of states for a ThC lattice without defects and also for the case with tetrahedral Th and $\langle 110 \rangle$ dumbbell interstitials. We note that one of the effects of the C $\langle 110 \rangle$ dumbbell is to introduce impurity states in the gap with energy between -4.5 eV and -6.5 eV. (see inset Fig. 9).

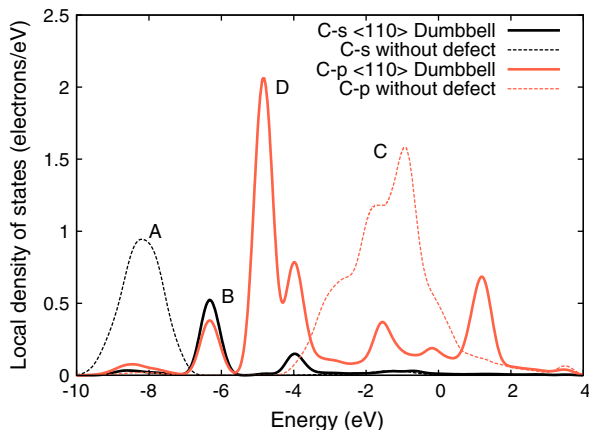


Fig. 6. PLDOSs at one of the C atom of a $\langle 110 \rangle$ dumbbell interstitial (solid lines) and for a C (dashed lines) atom in a 64 atoms lattice without defects.

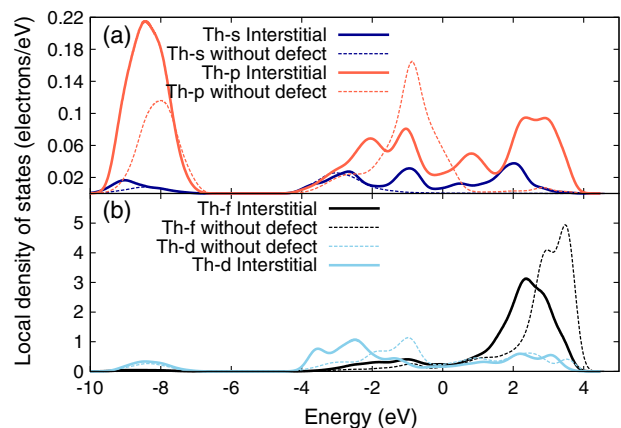


Fig. 8. PLDOSs at a Th tetrahedral interstitial (solid lines) and for a Th (dashed lines) atom in a 64 atoms lattice without defects.

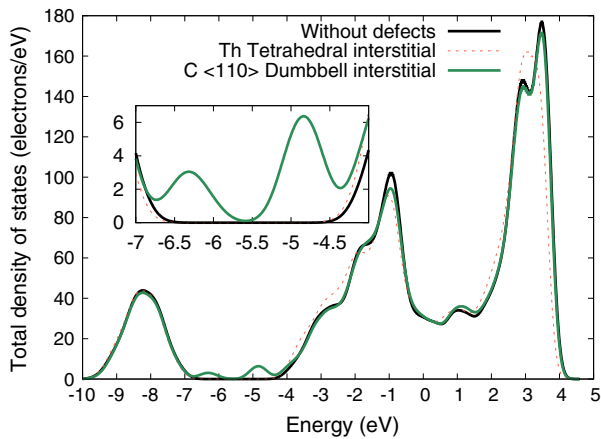


Fig. 9. Total densities of states of ThC for a 64 atoms lattice without defects and for Th at an interstitial tetrahedral site and for a carbon $\langle 110 \rangle$ dumbbell interstitial. (Inset) Zoom of the -4.5 eV to -6.5 eV region of the main panel.

4.3. Antisite defects

We analyze the effect of an antisite defect, which is given by the exchange of a C and a Th neighboring atoms. Calculating the formation energy is found that this type of defect is not stable. The initial configuration evolves, after relaxation, to a dumbbell one. The same behavior has been reported for UC [3].

4.4. Frenkel pairs

Finally, we obtain the formation energies of isolated and bound Frenkel pair for Th and C atoms. In the case of a bound Frenkel pairs the interstitial atom is in a tetrahedral position within the contiguous cube containing the vacancy (see Table 3). For isolated Frenkel pairs, we add the formation energy of a tetrahedral interstitial and of a single vacancy individually calculated in different supercells (see Eq. (4)).

In the case of thorium, we note that the bound Frenkel pair is more stable than the isolated one. The difference between the two Frenkel pairs is -0.23 eV, so that there is an effective attractive interaction between vacancy and interstitial defect. In the case of the bound pair, the Bader [25] charge of interstitial Th is 10.81 e, while in the isolated case it is 10.83 e. Both values are to be compared to the Bader charge of the perfect system, which is 10.19 e. The Bader charges of the surrounding atoms is also very similar in both cases. The same is observed for the surroundings of bound and isolated Th vacancy. These similarities point towards the very localized nature of the modifications induced by the defects. The difference in energy between bound and isolated Frenkel pairs can be traced back to a negative electrostatic contribution in the bound situation, this contribution goes to zero in the isolated case.

In the case of carbon Frenkel pairs the system relaxes towards a configuration formed by a $\langle 110 \rangle$ dumbbell-type interstitial and a vacancy. This is reasonable considering that the C $\langle 110 \rangle$ dumbbell interstitial is the most likely one among the carbon interstitials.

Table 3

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

	Thorium	Carbon
FP bound (eV)	9.89	–
FP isolated (eV)	10.12	3.67

5. Conclusions

In summary, we have performed a study of the stability of different point defects in ThC by means of first-principles calculations within the framework of DFT. We calculated the formation energy for vacancies, interstitial and Frenkel pairs. C isolated vacancies are the most likely defects in ThC, among the studied possibilities, while Th vacancies are highly unfavorable as compared to C ones. The formation energy of carbon vacancies is more than one order of magnitude smaller than the one corresponding to Th atoms. Carbon interstitials are also more probable than Th ones.

Among the possible C interstitial dumbbells those in the $\langle 110 \rangle$ direction are energetically preferred, they are followed by those along $\langle 100 \rangle$ and $\langle 111 \rangle$, in this order and are separated by 0.18 eV. On the other hand, the formation energy of a C tetrahedral interstitial demands nearly three times the energy needed for the other interstitials. When comparing with UC, the sequence appearing in the literature [3,4] for a C interstitial is the same as for ThC.

In the case of a thorium defect, the formation of tetrahedral interstitials is more likely than the formation of dumbbells, but among the possible dumbbells, those along $\langle 111 \rangle$ demand additional 0.38 eV than the tetrahedral interstitials. The formation of $\langle 110 \rangle$ dumbbells competes with the formation of Th monovacancies, while $\langle 100 \rangle$ dumbbells demand almost two times more energy than tetrahedral interstitials. It is interesting to observe that in the case of an U interstitial in UC, the formation of $\langle 111 \rangle$ dumbbells is more likely than tetrahedral ones [3,4].

As for Frenkel pairs, we have analyzed the tetrahedral case for Th, this is the energetically most stable in the case of a Th interstitial. We obtained that the formation energy of a bound Frenkel pair is smaller than for an isolated pair, contrary to what happens in the case of UC for U Frenkel pairs.

For a C Frenkel pair in the tetrahedral position, the bound defect is not stable and it relaxes forming a dumbbell type interstitial and a vacancy.

There are no important differences in the total DOSs of ThC with and without vacancies or with Th in a tetrahedral interstitial position at the low vacancy concentration considered. Only in the case of a C $\langle 110 \rangle$ dumbbell, impurity states appear in the gap which lies in the energy range going from -4.5 eV and -6.5 eV. The PLDOS of this dumbbell resembles the one of a C dimer.

This work is a first step in the study of defects in ThC, system for which there exists a nearly complete lack of experimental data. The investigation of the effect of incorporating fission products and of their migration is underway.

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