Diffusion in thorium carbide: A first-principles study

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HIGHLIGHTS

- Diffusion in thorium carbide by means of first-principles calculations is studied.
- The most favorable migration event is a C atom moving through a C-vacancy aided path.
- Calculated C atoms diffusion coefficients agree very well with the experimental data.
- For He, the energetically most favorable migration path is through Th-vacancies.

ARTICLE INFO

ABSTRACT

The prediction of the behavior of Th compounds under irradiation is an important issue for the upcoming Generation-IV nuclear reactors. The study of self-diffusion and hetero-diffusion is a central key to fulfill this goal. As a first approach, we obtained, by means of first-principles methods, migration and activation energies of Th and C atoms self-diffusion and diffusion of He atoms in ThC. We also calculate diffusion coefficients as a function of temperature.

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1. Introduction

The projects behind the future Generation-IV nuclear reactors [1] have boosted research on the possible materials to be used as nuclear fuels, among them thorium and its compounds (carbides and nitrides) [2,3]. The advantages of these compounds, compared to uranium ones, are: higher melting points, lower thermal expansion coefficients and larger thermal conductivities.

The study of thorium compounds in the context of nuclear fuels involves the prediction of their behavior under irradiation [4]. A first approach to this goal is the estimation of the migration paths, migration energies and diffusion coefficients. In particular, the study of self-diffusion and the diffusion of different incorporated elements.

The usual approach to study physical properties of materials is by means of first-principles calculations, for example, Lu et al. investigated the mechanical and thermodynamic properties obtained of ThN from lattice dynamics data [5]. Using an all-electron approach and local orbitals, Atta-Fynn and Ray obtained the structural, electronic and magnetic properties of the same compound [6]. 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 [7].

Shein et al. calculated structural parameters, electronic properties, X-ray emission (XES) and absorption (XAS) spectra [8] and elastic properties of ThC [9]. Structural, mechanical, electronic and thermodynamic properties of this Th compound were also investigated by Aydin et al. doing pseudopotential calculations for different exchange and correlation potentials within and beyond the usual local density approximation [10]. Lim and Scuseria obtained the structural parameters and electronic properties of the same Th compound using gaussian-type-orbitals within DFT and comparing with the results coming from the use of several types of functionals [11]. Sahoo et al. predicted a new high pressure structural sequence in ThC [12], while Guo et al. also studied ThC at high pressure [13]. Liao et al. obtained the lattice dynamics and the lattice thermal conductivity of ThC$_2$ and ThC [14].

In our previous works, we obtained the phonon spectrum, the mechanical and thermophysical properties [15], reported on the

energetics of several point defects [16] and studied the incorporation of He, Xe, Kr and O atoms in ThC [17].

The characteristics of the self-diffusion and of the diffusion of incorporated elements in ThC have not been yet, to the best authors' knowledge, theoretically obtained. It is not the case for compounds with similar structure. For instance, Ducher et al. calculated migration energies and diffusion paths in UC [18], Bévillon et al. obtained the activation energies of U and C in the case of self-diffusion and hetero-diffusion of fission products also in UC [19] and diffusion in ZrC was studied by Zheng et al. [20].

In this work, we report and analyze migration and activation energies and diffusion coefficients of Th and C in ThC, through different possible paths. We also study migration and activation energies of He atoms for their diffusion in ThC.

2. Calculation details

The electronic calculations are done within the framework of density functional theory (DFT) employing the Quantum ESPRESSO package [21]. The Generalized Gradient Approximation in the Perdew–Burke–Ernzerhof (GGA–PBE) formulation [22] is used for the exchange and correlation potential. This functional has already been proven to give accurate results in the cases of ThC [10,15–17], in Th [23] and UC [19], a carbide compound with a similar structure. This justifies the use of GGA instead of GGA + U. 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 [24], helium and xenon in UC [25] and xenon and krypton in UN [26]. The pseudopotential used for carbon is an ultrasoft one from the Quantum ESPRESSO pseudopotential library [27]. In the case of thorium, a norm-conserving Troullier–Martins [28] pseudopotential is generated with the *atomic* software of the same package following Ref. [23]. 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 [29]. The Brillouin zone is sampled by a $4 \times 4 \times 4$ k-point mesh using the Monkhorst–Pack [30] (MP) scheme for a 64 atoms supercell. This supercell size is enough to avoid spurious interactions due periodic feature of the simulations, as it has already checked in our previous works [15–17]. 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 [31] 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.

The nudged elastic band (NEB) [32] method is frequently used to find the minimum energy path (MEP) between an initial and final transition state. The MEP is found by optimizing a set of intermediate images of the system. The optimization is constrained by adding a spring interaction between adjacent images. Therefore, for each image the lowest energy possible configuration is found, while maintaining equal spacing to neighboring images. An improvement of this method is the climbing image NEB (CI-NEB) [33]. With this modification a rigorous convergence to a saddle point is obtained. The NEB and CI-NEB, as implemented in Quantum ESPRESSO, were used to calculate the migration energies, E_m, of thorium, carbon and helium atoms. For each case, we first use the NEB method and after a few iterations the image with the highest energy is identified. The CI-NEB procedure, is then used to find the final converged MEP.

3. Results and discussions

ThC is a metal [11] whose structure is of the NaCl-type (B1). The experimental equilibrium lattice parameter, a_0, is 5.335–5.344 Å

[3]. In our previous work [15], using the same pseudopotentials, we obtained $a_0 = 5.335$ Å.

In the following, we first discuss results obtained for self-diffusion of thorium and carbon in ThC, including migration and activation energies. Followed by the discussion of the diffusion coefficients. Finally, we analyze the diffusion of helium in ThC.

3.1. Self-diffusion

To analyze the self-diffusion of C and Th by means of NEB we consider interstitial and vacancy aided migration paths.

For C we obtain first the migration path between two tetrahedral interstitial positions through an octahedral interstitial site. It is found that the assumed saddle position, namely an octahedral site, is actually a minimum. The diffusing C atom forms a trimer (C–C–C) defect in the octahedral site. This behavior is similar to what has been found by Zheng et al. for C in ZrC [20]. Therefore, we consider migration between two trimer interstitial positions through a tetrahedral site (see Fig. 1, red circles). From the maximum in this migration path, which is the saddle point, the migration energy is obtained (see Table 1). The migration of a C atom to a first neighbor C-vacancy is also analyzed (see Fig. 1, green triangles). We obtained a migration energy of 2.0 eV, which is of the same order as the value obtained by Ducher et al. for UC [18]. The C-vacancy aided path is energetically more favorable than the interstitial one.

In Fig. 2 the relative energies of a Th atom moving between two tetrahedral interstitial positions through an octahedral site and from a Th to a neighboring Th-vacancy are shown. We note that these two paths have almost the same energetic barrier.

Using the migration energies, together with the formation energies, obtained in a previous work [16] (see Table 1), the activation energies given by

$$E_a = E_f + E_m, \tag{1}$$

for diffusion of Th and C through interstitial and vacancy paths, are calculated. These values are listed in Table 1.

A step forward in the study of diffusion is given by the calculation of the diffusion coefficients as a function of temperature. We
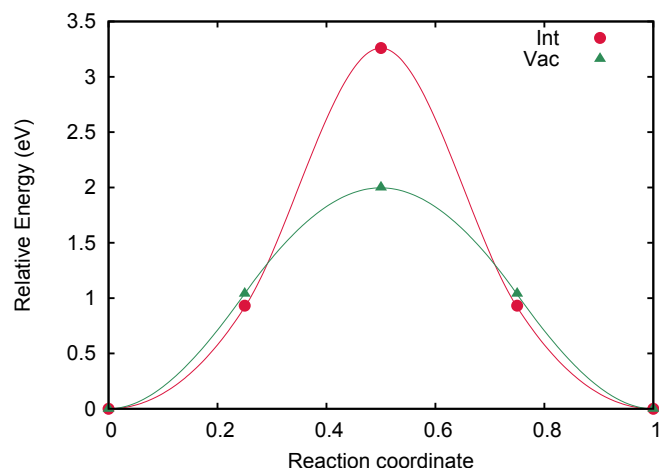

Fig. 1. Relative energy as a function of reaction coordinate, calculated with the CI-NEB method, for carbon migration through two paths: between two trimer octahedral positions through a tetrahedral position (red circles) and from a carbon site to a first neighbor vacancy site (green triangles). The energies are given 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 color in this figure legend, the reader is referred to the web version of this article.).

Table 1
Formation (E_f), migration (E_m) and activation (E_a) energies for C and Th self-diffusion.

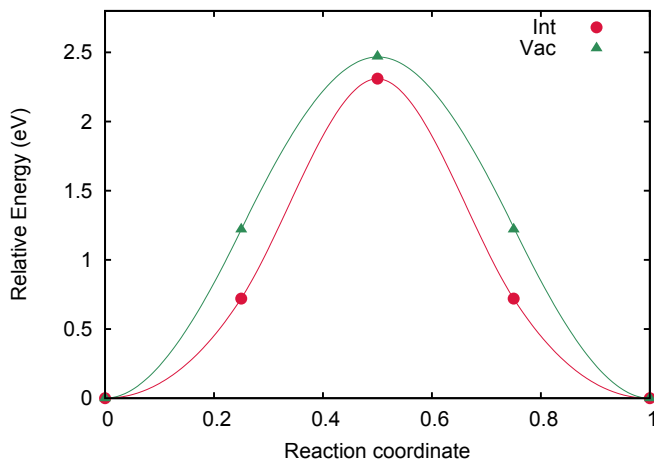| Atom-path	E_f (eV)	E_m (eV)	E_a (eV)
Th-Int	4.28	2.31	6.59
Th-vac	5.84	2.51	8.35
C-Int	2.11	3.25	5.36
C-vac	0.15	2.00	2.15

Fig. 2. Relative energy as a function of reaction coordinate, calculated with the CI-NEB method, for thorium migration through two paths: between tetrahedral positions through an octahedral position (red circles) and from a thorium site to a first neighbor vacancy (green triangles). 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 color in this figure legend, the reader is referred to the web version of this article.).

obtain these coefficients using the activation energies and the Arrhenius law,

$$D = D_0 \exp(-E_a/k_B T) \qquad (2)$$

where

$$D_0 = gfa_0^2 \nu \exp\left(\left(\Delta S_f + \Delta S_m\right)/k_B\right) \qquad (3)$$

where g is the geometric factor, f is the correlation factor, ν is the attempt frequency, ΔS_f is the entropy of defect formation and ΔS_m is the entropy of migration. In the case of a rock-salt structure, $g = 1$ and $f = 1$. The attempt frequency is approximated by a phonon Einstein frequency of 8.5 THz, this value was obtained in a previous work [15]. Following Zheng et al. [20] ΔS_f and ΔS_m are taken to be zero. We finally obtain that $D_0 = 2.42 \times 10^{-6}$ m²/s. In Fig. 3 diffusion coefficients as a function of temperature for C and Th atoms, through the migration paths considered, are presented. The results obtained for C diffusion through a carbon vacancy compare well with the available experimental data [34]. We note that diffusion coefficients for C defects are larger than for Th.

3.2. He diffusion in ThC

In this section we analyze the migration of helium in ThC. First, the migration energy of a helium atom through an interstitial path is obtained. This path is shown in Fig. 4(b), the initial and final states of this path are tetrahedral positions and the saddle-point is an octahedral site. In Fig. 5 we show the relative energies for this path and notice that the energy barrier of the octahedral saddle-point is of 0.88 eV. Similar values were reported by Pukari et al.
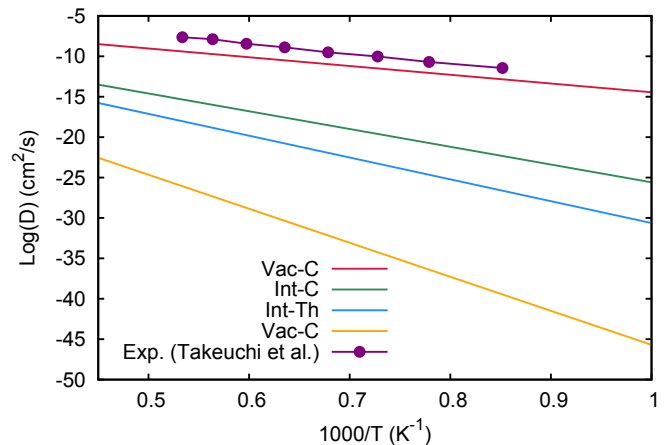

Fig. 3. Diffusion coefficients as a function of temperature for diffusion of C and Th atoms through interstitial and vacancy paths. We compare with experimental data for carbon diffusion in ThC [34].
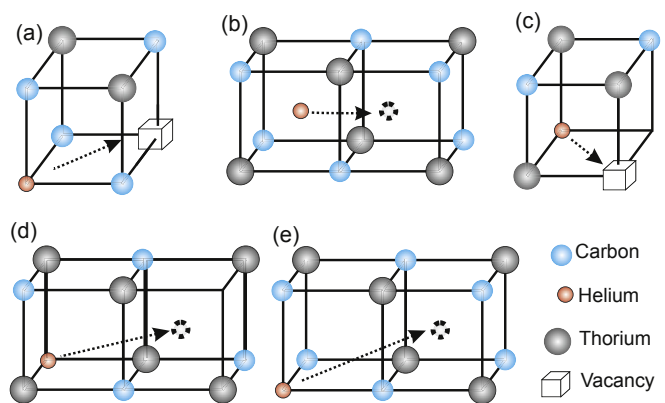

Fig. 4. He migration paths. (a) From a Th vacancy site to another one. (b) From one tetrahedral interstitial position to another, through an octahedral interstitial. (c) From a C vacancy site to another one. (d) From a C vacancy to a tetrahedral interstitial site. (e) From a Th vacancy to a tetrahedral interstitial site.

1.04 eV for He in ZrN [35] and by Yang et al. 0.77 eV for He in ZrC [36]. The migration energy of a He atom from a C(Th) substitution site to a C(Th) vacancy is also obtained (See Fig. 4)(a) and (b). The migration energy for these paths is shown in Fig. 5.

It is clearly seen that the migration through vacancies is energetically more favorable than through interstitial positions. We also note that the migration through vacancies of the FCC Th sublattice is the most favorable path among other vacancy-aided paths.

The release of helium from a C or a Th vacancy (see Fig. 4(d) and (e) respectively) to a tetrahedral interstitial position through an octahedral position is also considered. These migration paths have been studied in ZrN, that has the same structure as ThC [35]. In Fig. 6 we show the migration energy as a function of reaction coordinate for He moving from a C (red circles) or a Th (green triangles) vacancy to a tetrahedral interstitial site. The energetically most favorable path is the one starting at a C vacancy with a migration energy of 1.67 eV. In the case of a path starting at a Th vacancy the migration energy is 2.30 eV. In both cases, the migration energies from the interstitial tetrahedral positions to the vacancies are around 0.8 eV, as already obtained for the migration path between two tetrahedral positions through an octahedral one. These two migration energies are larger than He migration energies corresponding to vacancies-aided and interstitial paths.
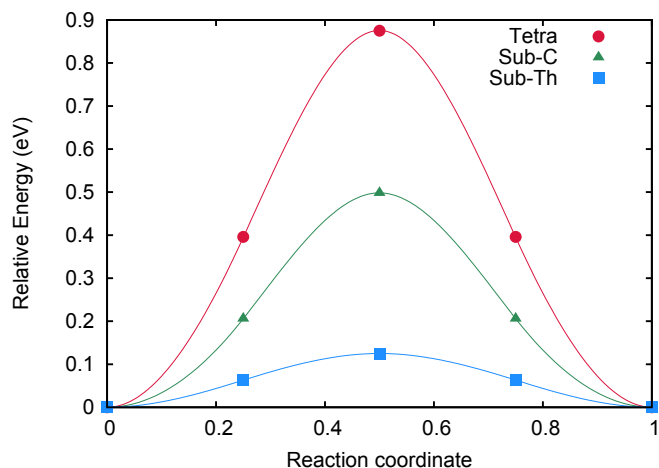
Fig. 5. Relative energy (eV) as a function of the reaction coordinate for He in ThC through three different paths. From a tetrahedral interstitial position to another one (red circles), from a C substitution site to a C first neighbor vacancy (green triangles) and from a Th substitution site to a Th first-neighbor vacancy (blue squares) one. 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 color in this figure legend, the reader is referred to the web version of this article.).
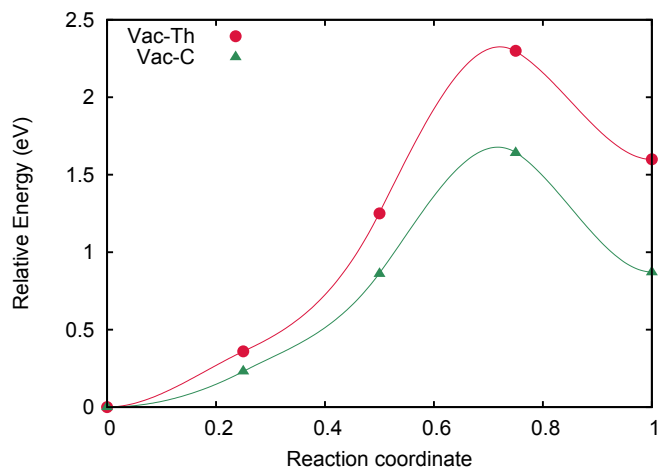

Fig. 6. Relative energy (eV) as function of the reaction coordinate for a He atom releases from a C or a Th vacancy. The energies are relative to the initial configurations. The lines are an interpolation of the path energy profile that goes exactly through each image.

4. Conclusions

In summary, we have studied diffusion processes in ThC by means of first-principles calculations within the framework of DFT and using the CI-NEB method. Migration energies for self-diffusion of Th and C atoms through interstitial and vacancy-aided paths have been obtained. The energetically most favorable migration event is the migration of C atoms through a C-vacancy aided path. We also calculated activation energies and obtained diffusion coefficients as a function of temperature. A good agreement with experimental data is attained for the self-diffusion of a C atom

through a C-vacancy aided path in ThC.

We have also studied the diffusion of helium atoms in ThC through interstitial and vacancy-aided paths concluding that the energetically most favorable migration path is the one through Th-vacancies.

Finally, we have analyzed the release of helium atoms from C or Th substitution sites. The release of helium from a C site is energetically most favorable, but this event requires more energy than migration energy through an interstitial path.

This work is a first approach to the study of diffusion in ThC, system for which there exists a nearly complete lack of experimental data. We hope that this results encourage to perform more experiments and calculations in ThC.

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