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Ab initio modeling of point defects, self-diffusion, and incorporation of impurities in thorium

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ABSTRACT

Research on Generation-IV nuclear reactors has boosted the investigation of thorium as nuclear fuel. By means of first-principles calculations within the framework of density functional theory, structural properties and phonon dispersion curves of Th are obtained. These results agreed very well with previous ones. The stability and formation energies of vacancies, interstitial and divacancies are studied. It is found that vacancies are the energetically preferred defects. The incorporation energies of He, Xe, and Kr atoms in Th defects are analyzed. Self-diffusion, migration paths and activation energies are also calculated.

1. Introduction

The Generation-IV nuclear reactor research, that has among its goals: enhanced safety and reliability, resistance to proliferation, reduced waste generation, improved economic competitiveness [1], has boosted the investigation of thorium as a nuclear fuel. Many reasons support this interest on thorium: world thorium reserves are estimated to be three to four times more abundant than the uranium reserves, thorium reactors generate less long lived radioactive waste than uranium reactors, lower risk of nuclear proliferation, and physical advantages, such as higher melting point and larger thermal conductivity than uranium [2–6].

The behavior under irradiation is a fundamental concern in the study of materials to be used as nuclear fuels [7]. A study on point defect and self-diffusion is a initial step in the way to understand this issue, that is central to have a full comprehension of the thermophysical and structural properties under irradiation. A next step in this path is the understanding of the consequence of the incorporation of fission products and He atoms, that are produced during the fission processes. This is important because fission products can lead to bubble formation, that is responsible for swelling and degradation of thermal conductivity across the fuel-clad gap.

First-principles calculations are very useful theoretical techniques to research these problems but in the case of thorium there are relatively few studies. Bouchet and Albers calculated the elastic constants at equilibrium volume and as a function of pressure [8]. Hu et al. reported on phase transition and thermodynamic properties within the framework of quasiharmonic approximation [9]. Bouchet et al. studied high-pressure lattice dynamics and thermodynamics properties [10]. Bouchet and Jomard also presented the phonon spectrum [11]. Richard et al. generated a Th pseudopotential and studied structural properties as a function of pressure [12]. In the case of point defects, self-diffusion, and incorporation of fission products, to the best of author's knowledge, there are not first principles calculations.

In this work, first principles calculations of structural properties and phonon spectrum of thorium are presented. The formation energies of point defects (vacancies, divacancies, and interstitials), atomic displacements and, charge transfers are presented. The incorporation energies of He, Xe, and Kr in vacancy, tetrahedral interstitial, or divacancy defects are obtained. Finally, migration and activation energies for self-diffusion through different possible paths are calculated.

2. Methodology

2.1. Computational details

Quantum ESPRESSO package [13], based on density functional theory, is employed for the first-principles calculations. The exchange and correlation potential is approximated by the Perdew–Burke–Erzenhof Generalized Gradient Approximation [14]. This approximation was used in Th attained very good results [8,9,11].

For thorium a norm-conserving Troullier–Martins [15] pseudopotential is generated with the *atomic* software from Quantum ESPRESSO package following Ref. [12]. This pseudopotential have already been used with very good results in ThC [16,17] and ThN [18].

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The pseudopotentials for helium, xenon, and krypton are norm-conserving ones from the Quantum ESPRESSO pseudopotential library [19].

A 32 atoms supercell, that avoid spurious interactions due periodic feature of the simulations, is used. The Monkhorst–Pack [20] scheme with a $4 \times 4 \times 4$ k-point mesh for integration in the Brillouin zone is chosen. Integrations are done with the Methfessel and Paxton [21] scheme and a smearing of 0.02 Ry. A 130 Ry energy cutoff is employed. The energy convergence as a function of energy cutoff and k-points' number is checked. The atomic positions are fully relaxed till forces are less than 0.03 eV/Å.

The approach to calculate the phonon dispersion curves is the self consistent density functional perturbation theory in the linear response approximation [22] as implemented in Quantum ESPRESSO, using for the dynamical matrices a $6 \times 6 \times 6$ q-point mesh.

The minimum energy path between an initial and final transition state is found by optimizing a set of intermediate images of the system by the nudged elastic band (NEB) [23] method. An improvement of this method is the climbing image NEB (CI-NEB) [24], that helps to obtain a more rigorous convergence of the saddle point. These methods, as implemented in Quantum ESPRESSO, are used to calculate the migration energies of thorium atoms.

2.2. Point defect formation and incorporation energies

The formation and incorporation energies are obtained following the expressions given by Freyss in Ref. [25],

(a) Vacancy formation energy

$$E_f^{VX} = E^{N-1} - E^N + E_{Th}, \tag{1}$$

where E^{N-1} is the energy of the supercell with a vacancy, E^N is the energy of the 32 atoms supercell without defects, and E_{Th} is the energy per atom of Th in a FCC structure.

(b) Interstitial formation energy (tetrahedral position):

$$E_f^{IX} = E^{N+1} - E^N - E_{Th}, \tag{2}$$

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

(c) Divacancy formation energy:

$$E_f^{VX} = E^{N-2} - E^N + 2E_{Th}, \tag{3}$$

where E^{N-2} is the energy of the supercell with two vacancies.

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

$$E_X^{Ivac} = E_X^{N-1} - E^{N-1} - E_X, \tag{4}$$

where E_X^{N-1} is the energy of the system with a He, Xe, or Kr atom incorporated in the vacancy and E_X is the energy of the isolated incorporated atom (He, Kr, or Xe).

(e) Incorporation energy of an atom of type X in a tetrahedral interstitial

$$E_X^{Iint} = E_X^{N+1} - E^N - E_X, \tag{5}$$

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

(f) Incorporation energy of an atom of type X in a divacancy site

$$E_X^{Idiv} = E_X^{N-2} - E^{N-2} - E_X, \tag{6}$$

where E_X^{N-2} is the energy of the system with a He, Xe, or Kr atom incorporated in the divacancy.

3. Results and discussions

3.1. Structural parameters and phonon dispersion curves

Thorium has an FCC crystal structure. The total energy as function of volume of this structure is calculated and fitting this curve with a fourth order Birch–Murnaghan equation of state [26] the equilibrium lattice parameter, a_0, and the bulk modulus, B_0, are obtained. These results are compared with experimental data [27–29] and with previous theoretical results [8,12,30] (see Table 1). The equilibrium lattice parameter and B_0 obtained in this work show a very good agreement with experimental and previous theoretical results.

The phonon dispersion curves calculated along several symmetry directions at zero pressure and zero kelvin conditions are shown in Fig. 1 (green lines), all the frequencies are positive showing the stability of the structure. These curves match very well with the experimental data obtained by inelastic-neutron-scattering measurements by Reese and Sinha [31] (blue dots). This phonon spectrum also has an excellent agreement with previous one calculated by Bouchet et al. [10].

These results are a good check of the performance of the Th

Table 1
Lattice parameter, a_0, and bulk modulus, B_0, for Th.

	a_0 (Å)	B_0 (GPa)
Experiments		
Armstrong et al. [27]	5.089	58
Greiner et al. [28]	5.085	60.37
Evans et al. [29]	5.081	58
Ab initio results		
Richard et al. [12]	5.051	54.2
Gupta et al. [30]	5.062	57.11
Bouchet et al. [8]	5.024	56
This work	5.045	57.04

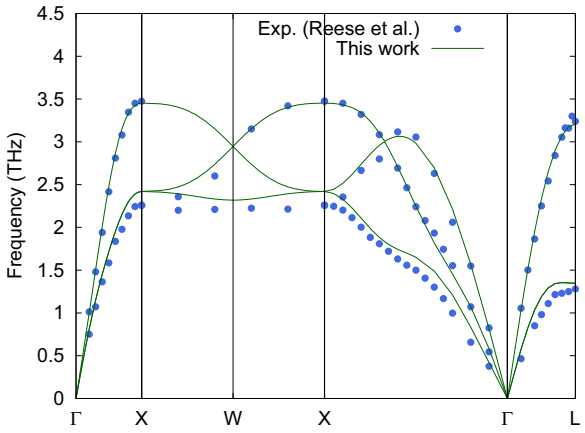

Fig. 1. (Color online) Phonon dispersion curves of Th calculated in this work (green lines) at equilibrium volume and T=0 K and experimental data (blue dots) from reference [31].

Table 2
Vacancy and tetrahedral interstitial formation energies of thorium and atomic displacement (δR) of first (1nn) and second (2nn) nearest-neighbor of the defect (Negative displacements are inward displacements).

Defect	E_f^{VX} (eV)	δR 1 nn (Å)	δR 2 nn (Å)
Vacancy	2.10	−0.06	0.0
Interstitial	5.45	0.55	0.0

Table 3
Divacancy formation energies (eV) along ⟨111⟩, ⟨110⟩, and ⟨100⟩ directions in thorium.

Direction	⟨111⟩	⟨110⟩	⟨100⟩
Divacancy	4.16	3.90	4.39

Table 4
Incorporation energies (eV) for He, Xe, or Kr atoms in Th FCC lattice at three incorporation sites (vacancy, divacancy and tetrahedral interstitial defects).

	Vacancy	Interstitial	Divacancy ⟨110⟩
He	0.78	2.36	0.079
Xe	1.59	8.81	0.98
Kr	1.77	7.34	0.95

pseudopotential.

3.2. Defects formation energies

The vacancy and interstitial formation energies of Th are given in Table 2. It is observed that is energetically easier to create Th vacancies than Th interstitial defect. It also easier to create a thorium vacancy in a FCC lattice than in thorium NaCl-type compounds like ThN (Th vacancy formation energy of 3.97 eV) [18] or ThC (Th vacancy formation energy of 5.84 eV) [17].

The only experimental data available for defect energy formation in Th is for vacancies. Kim et al. [32] estimated by trapping-model analysis of data measured by positron annihilation technique a value of 1.28 ± 0.23 eV. The difference with the value calculated in this work may be due to the approximations made in the analysis of the experimental data.

Vacancies produce almost no relaxation of the neighboring atoms, the inward displacement of first-nearest-neighbors is 0.06 Å. On the contrary, the tetrahedral interstitial defect induce a 0.55 Å outward displacement of the first-nearest-neighbors. Both types of defects do not distort the second-nearest-neighbors.

Formation energies of divacancies are presented in Table 3. The lowest energy configuration corresponds to the divacancy in the ⟨110⟩ direction, followed by ⟨111⟩ and ⟨100⟩ configurations. The interaction between vacancies within divacancy is analyzed by comparing its formation energy to the sum of the formation energy of two isolated vacancies. Vacancies in divacancies along ⟨100⟩ have a effective repulsive interaction due to the positive energy difference (0.19 eV) between isolated vacancies and divacancy formation energies. For divacancies along ⟨111⟩ and ⟨110⟩ directions, there is an effective attractive interaction as the difference between energies is negative

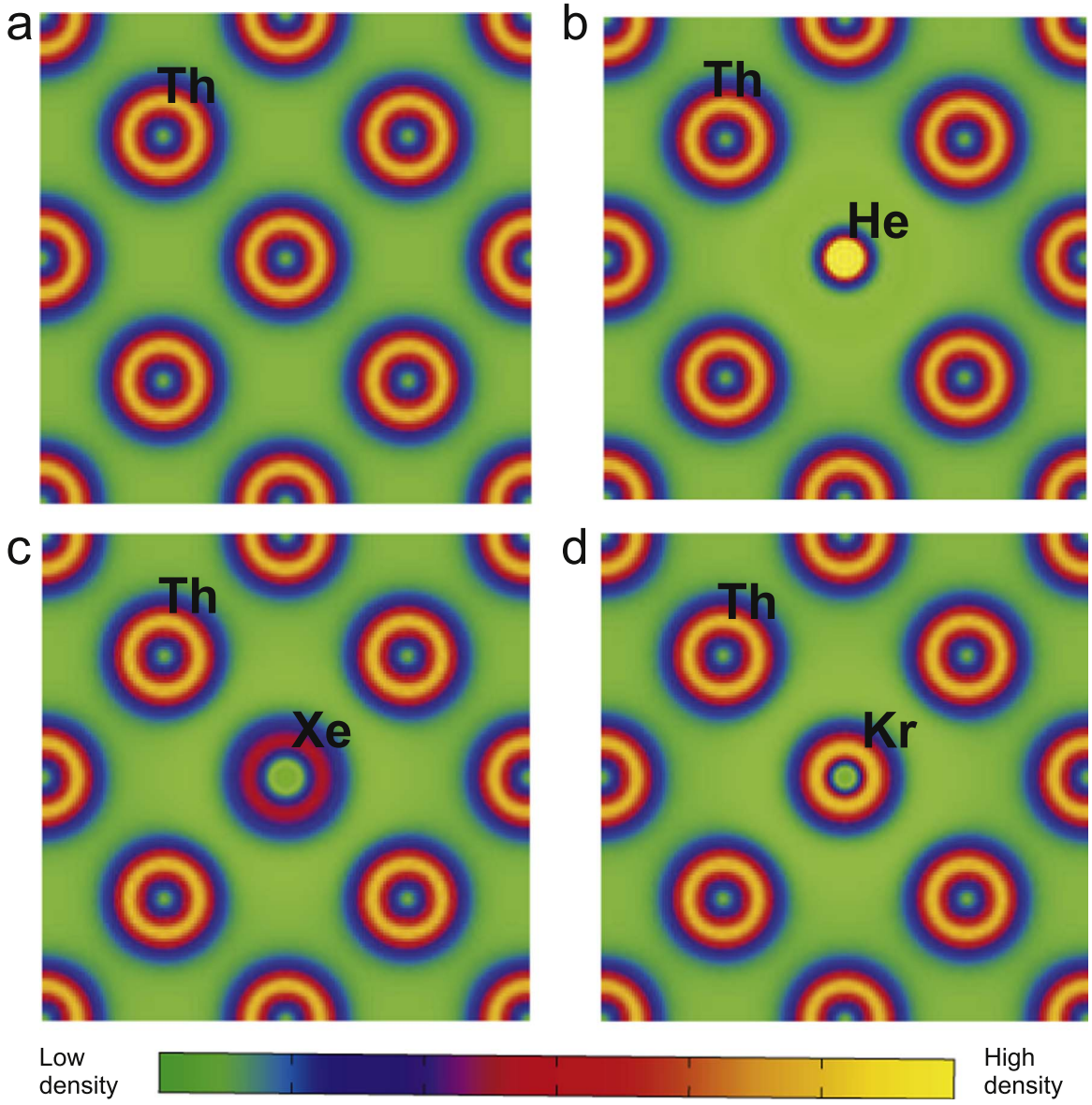

Fig. 2. Charge density contours plot in the (100) plane for (a) Th without defects. (b) Th with a He atom incorporated in a Th vacancy, (c) Th with a Xe atom incorporated in a Th vacancy, (d) Th with a Kr atom incorporated in a Th vacancy.

(⟨111⟩ − 0.04 eV, ⟨110⟩ − 0.3 eV).

3.3. Incorporation energies

The incorporation energies of He, Xe, and Kr atoms in three different sites (vacancies, tetrahedral interstitials, and divacancies along ⟨110⟩ are presented in Table 4). A lower energy indicates a most favorable incorporation site.

It is found that the most favorable incorporation site is the thorium divacancy along the ⟨110⟩ direction of the three incorporated atoms. This incorporation site is also the largest of the incorporation sites. The following incorporation site is the isolated thorium vacancy and the most unfavorable site is the tetrahedral interstitial. For uranium, it is observed a similar behavior. The incorporation atoms prefer to reside in the vacancy site rather in the interstitial site. Helium being the smaller atom is the one with the smaller incorporation energy for both vacancies and interstitials [33].

Incorporation of atoms can produce atomic displacements of the first nearest-neighbors of the incorporated atoms. He atom incorporated in a Th vacancy, after relaxation, induces an inward displacement of 0.023 Å of the first nearest-neighbor thorium atoms. Instead, Kr and Xe atoms produce negligible displacement of the first nearest-neighbor thorium atoms. This behavior is explained observing the size relation between incorporated atoms and Th atoms. Helium atom is six times smaller than thorium letting an inward displacement of the Th atoms occurs (in the case of a Th vacancy there is a 0.06 Å inward displacement). Kr and Xe atoms are larger avoiding this inward displacements. In the case of tetrahedral interstitial as incorporation site, He atom induces a 0.19 Å outward displacement, Kr atom a 0.43 Å and Xe atom a 0.52 Å, as the atomic radius are larger the displacements are larger.

The charge density contours plot in the (100) plane of Th without defects and with He, Kr, or Xe atoms incorporated in Th vacancy sites are shown in Fig. 2. As stated before, it is observed that the incorporation of these atoms in Th vacancies do not produce any distortions in the Th lattice.

Table 5
Bader analysis of the charge density of Th after the incorporation of He, Xe, and Kr in a Th vacancy, a Th divacancy and in a tetrahedral interstitial.

	Vac Th	Tetra Int	Divacancy
He	−0.1	−0.16	−0.09
Kr	−0.36	−0.50	−0.26
Xe	−0.53	−0.65	−0.39

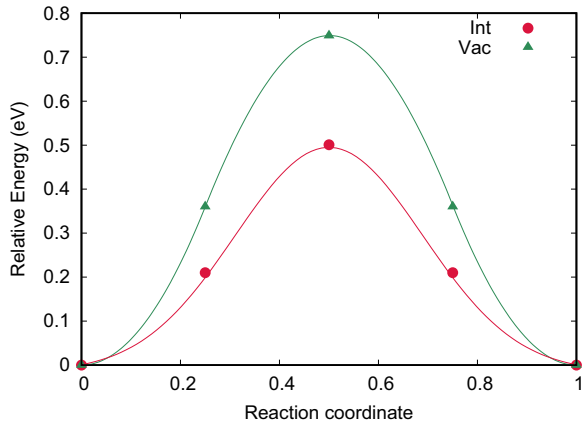

Fig. 3. (Color online) Relative energy as a function of reaction coordinate for a thorium atom moving: between two tetrahedral interstitial positions (red circles) and from a thorium site to a first neighbor vacancy (green triangles). The energy scale is relative to the initial configurations and lines are an interpolation of the path energy profile.

Table 6
Formation (E_f), migration (E_m) and activation (E_a) energies for Th self-diffusion throughout two paths.

Atom-Path	E_f (eV)	E_m (eV)	E_a (eV)
Th-Int	5.45	0.50	5.95
Th-Vac	2.10	0.75	2.85

In Table 5 the Bader [34] analysis of Th with the incorporation of He, Xe, or Kr in different defects are presented. There is a very small charge transfer for He incorporated in any of the three considered sites. In the case of Kr and Xe, the charge transfer is larger in the tetrahedral interstitial as incorporation site. For the three elements, the charge transfer in the case of a divacancy is smaller than in a single vacancy.

3.4. Self-diffusion

The self-diffusion of Th by means of NEB considering interstitial and vacancy aided migration paths is calculated (see Fig. 3). The Th-interstitial aided path is energetically more favorable than the vacancy one. From the maximum in this migration path, which is the saddle point, the migration energy is obtained (see Table 6).

The activation energy, E_a, which is given by

$$E_a = E_f + E_m, \tag{7}$$

is calculated in the cases of diffusion of Th through interstitial and vacancy paths (see Table 6). In the literature are two measurement of E_a, one by Schmitz and Fock [35] of 3.10 ± 0.1 eV and another of 3.36 eV reported in [36]. The difference between the activation energy calculated in this work with the one measured by Schmitz and Fock is 0.25 eV that is almost the same difference between the two measured results.

4. Conclusions

Structural parameters and phonon dispersion curves of Th were calculated within the framework of DFT. These results are in good agreement with experimental and previous theoretical ones.

The formation energy of vacancies, interstitials, and divacancies were obtained. It was found that Th isolated vacancies are the most likely defects in Th, for the three kind of defects analyzed. Th divacancies in the ⟨110⟩ direction are energetically preferred, followed by those along ⟨111⟩ and ⟨100⟩ configurations.

The incorporation energies of helium, xenon, and krypton atoms in defects (vacancies, tetrahedral interstitials, and divacancies along the ⟨110⟩ direction) of the thorium FCC lattice were studied. Atomic displacements, charge transfer, and charge density were analyzed. For He, Xe, and Kr, the energetically most favorable site is the divacancy defect along ⟨110⟩. The charge transfer in the case of incorporated He atoms is very weak. For Kr and Xe, the charge transfer is larger in the case of incorporation in a interstitial position.

Through NEB calculations migration paths and energies for Th atoms through interstitial and vacancy were obtained. The energetically most favorable migration path is through a interstitial one. The activation energies were also calculated. A good agreement with experimental data is attained for activation energy of self-diffusion through a Th-vacancy aided path.

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