



Phonon spectrum, mechanical and thermophysical properties of thorium carbide

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ABSTRACT

In this work, we study, by means of density functional perturbation theory and the pseudopotential method, mechanical and thermophysical properties of thorium carbide. These properties are derived from the lattice dynamics in the quasi-harmonic approximation. The phonon spectrum of ThC presented in this article, to the best authors' knowledge, have not been studied, neither experimentally, nor theoretically. We compare mechanical properties, volume thermal expansion and molar specific capacities with previous results and find a very good agreement.

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1. Introduction

Thorium-based materials are currently being investigated in relation with their potential utilization in Generation-IV reactors [1]. In comparison with previous uranium-based fuels, thorium-based ones have many additional physical advantages, such as higher melting points, higher corrosion resistivity, lower thermal expansion coefficients and larger thermal conductivity. In order to develop the technologies for the nuclear cycle based on oxide, nitride or carbide fuels, it is important to describe and to understand their thermophysical and mechanical properties.

In recent years there have been several first-principles studies of thorium and its compounds. For example: Richard et al. [2] have generated a pseudopotential and investigated the crystal structure of thorium. For this material Bouchet et al. [3] have presented results of high-pressure lattice dynamics and thermodynamic properties using Density Functional Theory (DFT) and the pseudopotential method. Also for thorium, Hu et al. [4] have reported on a first-principles study of the phase transition and thermodynamic properties. Likewise, Jaroszewicz et al. [5] have derived an interatomic pair potential for thorium by using Chen-Möbius inversion of cohesive energy. With this interatomic potential they have calculated [6], elastic and thermal properties. For thorium dioxide, Lu et al. [7] have investigated the thermodynamic properties and structural stabilities by means of DFT and lattice dynamics. Similarly, Wang et al. [8] have obtained mechanical properties, electronic structure and phonon dispersion of ground state thorium dioxide as well as the structure behavior until high-pressures using first-principles calculations. Based on DFT Lu et al. [9] investigated

electronic structure; mechanical and thermodynamic properties derived from lattice dynamics data of thorium nitride. Modak and Verma [10] have studied the electronic properties, phonon dispersion relations, elastic constants, structural phase transitions of ThN by means of pseudopotential DFT methods. With the full-potential all-electron linearized augmented plane wave plus local orbital method Atta-Fyn and Ray [11] obtained the structural, electronic and magnetic properties of ThN. In the case of ThC, structural, mechanical, electronic and thermodynamic properties were investigated by Aydin et al. [12] by means of plane-wave pseudopotential calculations with GGA, LDA and LDA+U. Lim and Scuseria [13] have studied structural parameters and electronic properties of ThC using gaussian-type-orbitals and density functional theory with several types of functionals. With the full-potential linearized augmented plane wave method Shein et al. have investigated structural parameter, electronic properties, and spectra of X-ray emission (XES) and absorption (XAS) [14] and elastic properties [15] of ThC. Unlike Th, ThN and ThO₂, the vibrational properties of ThC, to the best authors' knowledge, have not been studied, neither experimentally, nor theoretically.

In this work, we present a study of thermophysical and mechanical properties of ThC derived from the lattice dynamics in the quasi-harmonic approximation (QHA) [16] by using density functional perturbation theory and the pseudopotential method.

2. Method of calculations

2.1. Electronic and phononic calculations

The electronic and phononic calculations are done within the framework of DFT employing the Quantum ESPRESSO package [17]. The Generalized Gradient Approximation in the

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Perdew–Burke–Erzenhof (GGA-PBE) formulation [18] is used for the exchange and correlation potential. The pseudopotential for carbon is an ultrasoft one from the Quantum ESPRESSO pseudopotential library [19]. In the case of thorium, a norm-conserving Troullier and Martins [20] pseudopotential is generated with the *atomic* software of the Quantum ESPRESSO package following Ref. [2]. The Brillouin zone is sampled with a $12 \times 12 \times 12$ k -point mesh using the Monkhorst and Pack [21] (MP) scheme. A 250 Ry cutoff is used. The Brillouin zone integrations are carried out with the Methfessel and Paxton [22] scheme and a smearing of 0.02 Ry. These parameters ensure that errors in the calculated total energy are less than 0.1 mRy/at.

The phonon dispersion curves are obtained within the framework of self consistent density functional perturbation theory (DFPT) in the linear response approach [23] as implemented in Quantum ESPRESSO. The dynamical matrices are calculated on a $6 \times 6 \times 6$ q -point MP mesh.

2.2. Elastic constants

The elastic constants give information on the stability and mechanical properties of solids by describing the behavior of crystals under elastic deformations. There are only three independent elastic constants in a cubic material, C_{11} , C_{12} and C_{44} . In this work, the elastic constants are obtained from the slopes of the acoustic phonon branches in the long wavelength limit [24]. The bulk modulus B_0 , shear modulus G , Young's modulus E , Poisson's ratio ν and anisotropy parameter A are obtained using following relations:

$$B_0 = \frac{1}{3}(C_{11} + 2C_{12}) \quad (1)$$

$$G = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (2)$$

$$E = \frac{9B_0G}{3B_0 + G} \quad (3)$$

$$\nu = \frac{3B_0 - E}{6B_0} \quad (4)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (5)$$

2.3. Thermodynamic functions

The total free energy for a metallic system can be expressed as the sum of the electronic and phononic contributions [25]. We assume that all temperatures of interest in this work are well below the electronic energy range and we have neglected the contribution of electronic excitations. In the quasi-harmonic approximation [16], which takes into account the volume dependence of the phonon frequencies, the Helmholtz free energy is expressed as

$$F(V, T) = E_e(V) + F_{ph}(V, T), \quad (6)$$

where E_e is the electronic contribution at $T = 0$ K and F_{ph} is the phonon contribution to the Helmholtz free energy

$$F_{ph}(V, T) = k_B T \sum_{j\mathbf{q}} \ln[2 \sinh(x)], \quad (7)$$

where $x = (\hbar\omega_j(\mathbf{q})/2k_B T)$ and $\omega_j(\mathbf{q})$ is the frequency of the j th phonon mode at point \mathbf{q} in the Brillouin Zone (BZ). The sum is over the BZ.

The vibrational contribution to the isochoric heat capacity C_V is directly calculated through

$$C_V(T) = k_B \sum_{j\mathbf{q}} x^2 \frac{1}{\sinh^2(x)}. \quad (8)$$

The equation of state is obtained by

$$P(V, T) = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial E}{\partial V} - \sum_{j\mathbf{q}} \frac{\hbar}{2} \frac{\partial \omega_j(\mathbf{q})}{\partial V} \coth(x), \quad (9)$$

to calculate pressure with Eq. (9) we must obtain the volume dependence of $\omega_j(\mathbf{q})$. Therefore, we calculate phonon dispersion curves for several volume around the $T = 0$ K equilibrium volume.

The volume thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_T. \quad (10)$$

The partial Grüneisen parameter, related with the anharmonicity of individual phonons is

$$\gamma_j(\mathbf{q}) = -\frac{V}{\omega_j(\mathbf{q})} \frac{\partial \omega_j(\mathbf{q})}{\partial V}, \quad (11)$$

and the overall Grüneisen parameter is the weighted average of $\gamma_j(\mathbf{q})$ with C_V

$$\gamma = \frac{1}{C_V} \sum_{j\mathbf{q}} \gamma_j(\mathbf{q}) C_V(j, \mathbf{q}). \quad (12)$$

The anharmonicity introduced by the volume dependence of the phonon frequencies allows us to differentiate C_p from C_V . Therefore, C_p , which is what experiments determine directly, is calculated with C_V , γ and α_V by the equation

$$C_p = C_V(1 + \alpha_V \gamma T). \quad (13)$$

The Debye Temperature $\Theta_D(T)$ is obtained from the elastic constants using the average sound velocity v_m by equation [6]

$$\Theta_D^{el} = \frac{\hbar}{k_B} \left[\frac{3n}{4\pi V} \right]^{1/3} v_m, \quad (14)$$

where n is the number of atoms in the unit cell. We also calculate $\Theta_D(T)$ fitting C_V with the Debye approximation for low temperature

$$C_V = \frac{12\pi^4 n k_B T^3}{5\Theta_D^3}. \quad (15)$$

3. Results and discussions

The structure of ThC is a NaCl-type (B1). This structure has only two atoms in its primitive cell. The equilibrium lattice parameter a_0 , the bulk modulus B_0 and its derivative B'_0 in this structure are obtained by fitting the total energy (Fig. 1) with a fourth order Birch–Murnaghan equation of state [26]. We compare our results with experimental data [27–29] and with previous theoretical results [12–14] (see Table 1); all these works use the GGA-PBE for

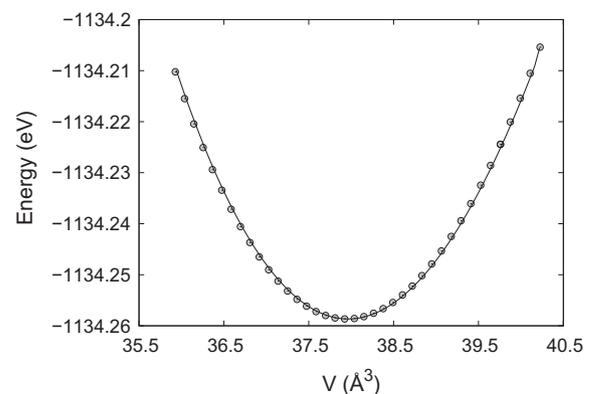


Fig. 1. Total energy as a function of volume fitted with a fourth order Birch–Murnaghan equation of state at 0 K for ThC.

Table 1

Lattice parameter a_0 , bulk modulus B_0 and its derivative B'_0 comparison between experimental and theoretical results.

	a_0 (Å)	B_0 (GPa)	B'_0
This work	5.335	134.78	3.001
Exp.	5.344 [27]	109 [28], 125 [29]	3.1 [28]
Aydin et al. [12]	5.341	134.33	3.071
Shein et al. [14]	5.388	131.89	2.73
Lim et al. [13]	5.340	132.21	2.88

the exchange and correlation potential. Our calculated equilibrium lattice parameter and B'_0 show a very good agreement with the experimental and previous theoretical results. The calculated bulk modulus differs with the experimental ones by between 7% [29] and 24% [28] but it is in very good accordance (a difference of less than 2.2%) with other theoretical results [12,14,13].

In Fig. 2 we show the relative volume as a function of pressure as calculated with the Murnaghan equation of the state [26] using the parameters of Table 1 (black line). We compare this result with experimental data from Ref. [30] (full black circles). We also compare with the results obtained through a structural relaxation using the Broyden–Fletcher–Goldfarb–Shanno method as a function of pressure (open circles). For pressures below 10 GPa the calculated volume shows an excellent agreement with the experimental one and for larger pressures the observed difference is less than 2%; which gives confidence to the selected pseudo-potentials.

In Fig. 3 we display the phonon dispersion curves as calculated along several symmetry directions at zero pressure and zero kelvin conditions. We observe six phonon modes (3 acoustic and 3 optics branches) in the dispersion relations, this is in accordance with a primitive cell with two atoms. We indicate the transverse and longitudinal branches of the phonon dispersion curves. We stress that all the frequencies are positive showing the stability of the structure.

The elastic constants, derived from the acoustic branches of the phonon spectrum, and related magnitudes (Eqs. (1)–(5)) are summarized in Table 2. The mechanical stability criteria leads to the following restrictions on the elastic constants $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{12} < B_0 < C_{11}$ [31]. All of them are satisfied for our calculated elastic constants. These results are compared with previous works and the best agreement is with the FLAPW-GGA results of Shein et al. [15]. We point out that the bulk modulus derived from the elastic constants differs in just 2.7% with the one calculated with the fitting procedure (see Table 1). This

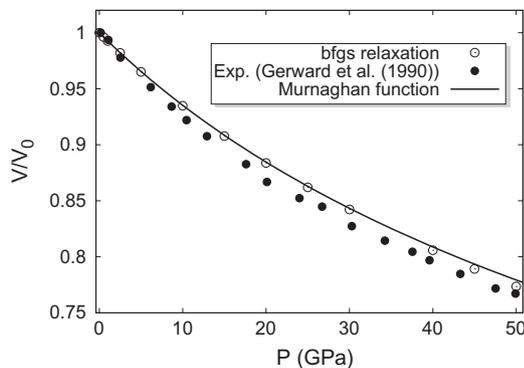


Fig. 2. Relative volume as a function of pressure for ThC at $T = 0$ K. We compare the experimental data [30] (full black circles) with the values obtained with a Broyden–Fletcher–Goldfarb–Shanno structural relaxation (bfgs) (open circles) and with the values calculated with the Murnaghan equation of state using the parameters of Table 1 (black line).

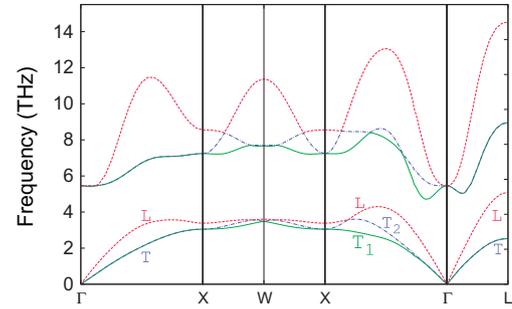


Fig. 3. Calculated phonon dispersion curves for B1 ThC at equilibrium volume and $T = 0$ K.

Table 2

Elastic constants and related magnitudes for ThC at $T = 0$ K.

	This work	Shein et al. [15]	Aydin et al. [12]
C_{11} (GPa)	222.10	252.2	276.4
C_{12} (GPa)	85.67	96.3	87.2
C_{44} (GPa)	66.12	60.2	99.1
B_0 (GPa)	131.15	148.3	158.2
G (GPa)	67.10	66.7	87.8
E (GPa)	171.97	174.1	222.2
ν	0.28	0.30	0.27
A	0.97	0.77	0.98

validates the elastic constants calculated from the phonon dispersion curves.

We calculate the Debye temperature from the elastic constants using Eq. (14), $\Theta_D^{\text{el}} = 311$ K. Another procedure to calculate Θ_D is by fitting C_V in the low temperature range, with the low temperature limit of the C_V 's Debye approximation (Eq. (15)). This yields $\Theta_D = 298$ K. These two values are in good agreement. We compare this last Θ_D with the one quoted by Harnes et al. [32], $\Theta_D = 280$ K, and they differ by less than 6.4% and with the one reported by Danan [33], $\Theta_D = 262$ K the differ by less than 13.7%. The experimental results for Θ_D were obtained on basis of C_p measurements.

The PDOS and the projected PDOS are plotted in Fig. 4. The integration over the Brillouin zone has been performed with the tetrahedron method [34]. There is only a little overlap between the projected PDOS for thorium and carbon. We observe that the PDOS is almost split into two: the range of 0–5 THz (mostly acoustic vibrations) where the vibrations of thorium atoms are dominant and the range of 5–24 THz (optic vibrations) where the vibrations are mainly due to carbon atoms. This behavior is related to the much higher weight of thorium with respect to carbon.

In the Einstein model of lattice dynamics the optical phonons are represented by a set of independent oscillators with the same

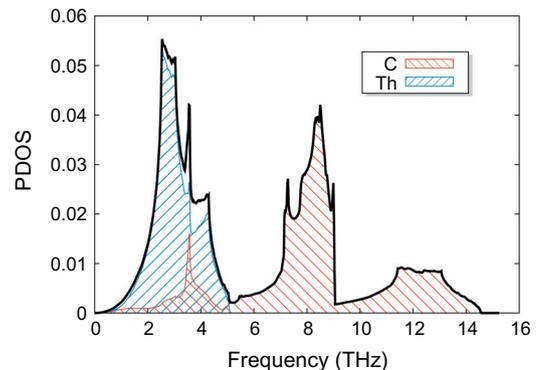


Fig. 4. Phonon density of states and projected PDOS for B1 ThC at equilibrium volume and $T = 0$ K.

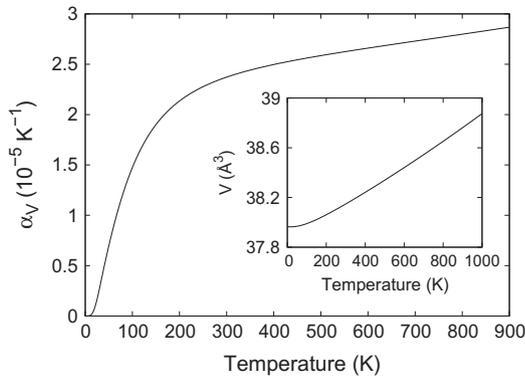


Fig. 5. Volume thermal expansion α_V as a function of temperature for ThC. (Inset) Volume as a function of temperature at zero pressure.

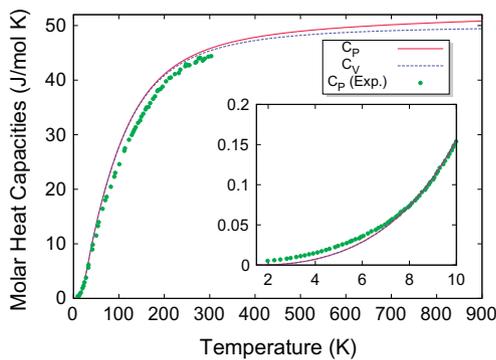


Fig. 6. Molar heat capacities of ThC. C_V (blue dashed line) derived from phonon frequencies as a function of temperature. C_P calculated in this work (red line) and from reference [33] (green dots). (Inset) Zoom of the low temperature range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

frequency (Einstein's frequency, ν_E). From the optical range of the PDOS we associate the peak at 8.5 THz with ν_E . This value is compared with the optical-phonon frequency 9.3 THz, measured by neutron scattering [35], and with frequency 9.73 THz, obtained by Danan [33], from the Einstein temperature in his measures of C_P .

In Fig. 5 we present the volume thermal expansion α_V as a function of temperature calculated from Eq. (10). This $\alpha_V(T)$ has an excellent agreement with the one present by Aydin et al. [12]. In reference [36] it has been reported a value for the average linear thermal expansion, $\alpha_l = 6.53 \times 10^{-6} \text{ K}^{-1}$ (using that $\alpha_V = 3\alpha_l$ we get $\alpha_V = 1.959 \times 10^{-5} \text{ K}^{-1}$) between 291 K and 1114 K obtained by X-ray diffraction. Our average value of α_V for the same range of temperature is $2.72 \times 10^{-5} \text{ K}^{-1}$ showing a good agreement. For measurements between 974 K and 1174 K Satow [37] reports $\alpha_l = 8.5 \times 10^{-6} \text{ K}^{-1}$ ($\alpha_V = 2.55 \times 10^{-5} \text{ K}^{-1}$). Our average α_V for this temperature range is $2.99 \times 10^{-5} \text{ K}^{-1}$. In the inset of Fig. 5 we show the temperature dependence of the volume obtained from equation of state (Eq. (9)). By means of differentiating this curve we calculate α_V .

In Fig. 6 we present the molar heat capacity C_V derived from phonon frequencies (Eq. (8)). We also plot the C_P calculated with Eq. (13) and the experimental result of C_P measured by Danan [33]. In the inset we show a zoom of the low temperature range. In this range we note a very good agreement with the experimental result. We also observe the expected difference between C_V and C_P

for high temperatures as well as the convergence of C_V to the Dulong–Petit's limit.

4. Conclusion

In summary, we have performed a description of the structural parameters, and of the mechanical and thermophysical properties of ThC. These are essential data for the knowledge of any material and in particular and very specially in the case of nuclear fuel materials. The mechanical and thermophysical properties were obtained from the relation dispersions. Even though phonon spectra are experimentally and/or numerically known for most of the materials used or proposed as nuclear fuels, this is not the case for ThC. To the best authors' knowledge, we have presented the first calculation of phonon dispersion curves of ThC. The elastic constants, volume thermal expansion coefficients and the molar heat capacities C_V and C_P , derived from the dispersion relations are in good agreement with experimental and previous theoretical ones. The lack of experimental data (e. g. elastic constants, phonon spectrum) in the case of ThC turn our calculations suitable for comparisons with previous results which use another calculation procedure [12]. Likewise, we hope that these results encourage to perform experiments to obtain the phonon spectrum and elastic constants of ThC.

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