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First-principles study of structural, elastic and electronic properties of thorium dicarbide (ThC_2) polymorphs

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ABSTRACT

The comparative study of the structural, elastic, cohesive and electronic properties of three polymorphs (α-monoclinic, β-tetragonal and γ-cubic) of thorium dicarbide ThC_2 is performed within the density-functional theory. The optimized atomic coordinates, lattice parameters, theoretical density (ρ), bulk moduli (B), compressibility (β), as well as electronic densities of states, electronic heat capacity (γ) and molar Pauli paramagnetic susceptibility (χ) for all ThC_2 polymorphs are obtained and analyzed in comparison with available experimental data. The peculiarities of inter-atomic bonding for thorium dicarbide are discussed. Besides, we have evaluated the formation energies (E_f) of ThC_2 polymorphs for different possible preparation routes (namely for the reactions with the participation of simple substances (metallic Th and graphite) or thorium monocarbide ThC and graphite). The results show that the synthesis of the ThC_2 polymorphs from simple substances is more favorable – in comparison with the reactions with participation of Th monocarbide.

1. Introduction

The binary compounds formed by thorium with light *sp* elements possess high density, good thermal conductivity and some other interesting physical properties which makes them attractive from a fundamental point of view as well as for a variety of technical applications for example as alternative fertile materials to be used in nuclear breeder systems *etc*, see [1–4]. The thorium carbides belong to this important group of materials.

Thorium reacts with carbon to form the two main phases. One of them is thorium monocarbide (ThC), which crystallizes in the cubic $B1$-like structure, where carbon atoms occupy the octahedral interstitial sites in the face-centered cubic thorium sublattice. This phase is stable over a wide range of C/Th compositions (ThC_x where $1.0 \geqslant x > 0.55$ [3]), *i.e.* can possess the high carbon deficiency.

The second phase is carbon-rich thorium dicarbide ThC_2, with relatively narrow range of homogeneity. Thorium dicarbide exists as stoichiometric (C/Th = 2) phase in three polymorphic modifications: low-temperature α-ThC_2 polymorph (up to 1700 K) and two high-temperature polymorphs: β-ThC_2 (in range $1700\ K < T < 1754\ K$) and γ-ThC_2 (at $T > 1754\ K$), see [3,5,6].

The physical properties and chemical behavior exhibited by the thorium carbides are closely related to their electronic structure. Today, a set of the theoretical studies have been performed to understand the electronic structure and the origin of properties of thorium monocarbide ThC [3,7–13]. As distinct from the cubic Th monocarbide, the data on the fundamental electronic properties for ThC_2 polymorphs are very limited. To our knowledge, up to now only the structural and electronic parameters for low-temperature modification α-ThC_2 were studied theoretically using the density-functional theory [11].

In this work. we present the results of *ab initio* study of the structural, elastic, and electronic properties of all three α, β and γ ThC_2 polymorphs. As a result, the equilibrium geometries, theoretical density (ρ), bulk moduli (B) and compressibility (β), electronic densities of states (DOS), the Sommerfeld constant (γ) and the Pauli paramagnetic susceptibility (χ) for all mentioned polymorphs are obtained for the first time and analyzed in comparison with available experimental data. Additionally, the theoretical estimations of the formation energies for ThC_2 polymorphs which can provide the important insights of the fundamental aspects of phase equilibrium in the Th–C system are performed. The peculiarities of the chemical bonding in thorium dicarbide are also discussed.

2. Models and method of calculation

The common structural feature of all ThC_2 polymorphs is that these materials include in their crystal frameworks the discrete C_2 structural units – so-called C_2 dumbbells, see Fig. 1.

The low-temperature α modification of ThC_2 has a monoclinic structure (space group $C2/c$) with four formula units in elementary cell ($Z = 4$); the cell structure and the orientation of the C_2 dumbbells are illustrated in Fig. 1. The intermediate β modification of ThC_2 has a body-centered tetragonal structure (space group

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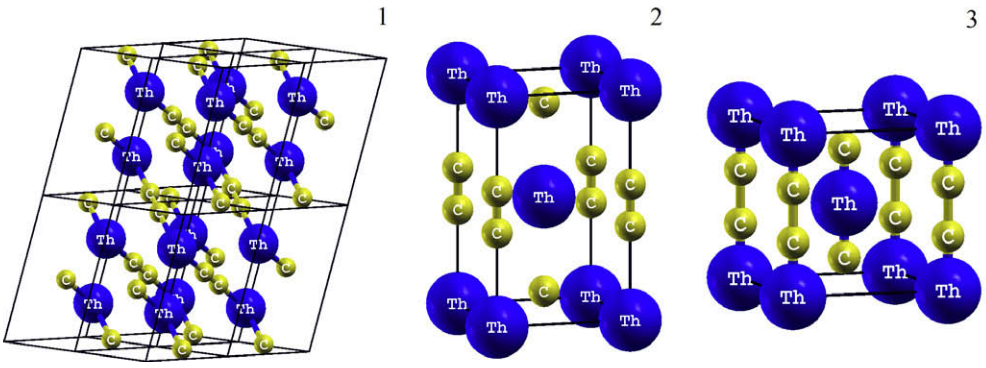

Fig. 1. Atomic structures of ThC_2 polymorphs: (1) monoclinic α-ThC_2; (2) tetragonal β-ThC_2 and (3) cubic γ-ThC_2.

I4/*mmm*, $Z = 2$) where the C_2 dumbbells are oriented along the *c* axis. Finally, the high-temperature γ modification of ThC_2 crystallizes in a face-centered cubic structure (KCN-structural type, space group F*m*3*m*, $Z = 4$), see Fig. 1.

The band-structure calculations of the all mentioned ThC_2 polymorphs were done by means of the density-functional theory (DFT) and the Vienna *ab initio* simulation package (VASP) [14,15] in projector augmented waves (PAW) formalism [16,17] and spin–orbit interactions. Exchange and correlation were described by a nonlocal correction for LDA [18] in the form of the generalized gradient approximation (GGA) [19]. The kinetic energy cutoff of 600 eV and *k*-mesh of 8 × 8 × 8 were used. The geometry optimization was performed with the force cutoff of 1 meV/Å.

3. Results and discussion

3.1. Structural and elastic properties

As the first step, the total energy (E_{tot}) *versus* cell volume calculations were carried out to determine the equilibrium structural parameters for considered ThC_2 polymorphs and their relative stability. These calculations were performed with full-lattice optimization including atomic coordinates. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 0.01 meV as calculated at consecutive steps.

Fig. 2 shows the variation for E_{tot} from cell volume *V*; the calculated equilibrium lattice constants and atomic positions are given in Table 1. The results obtained allow us to make the following conclusions.

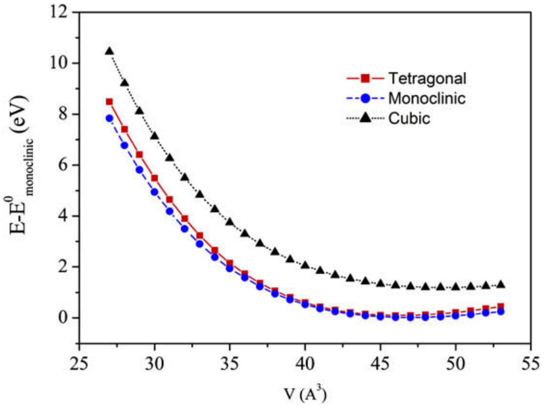

Fig. 2. Energy minimization with respect to cell volumes for ThC_2 polymorphs: monoclinic α-ThC_2, tetragonal β-ThC_2 cubic γ-ThC_2. The values of the total energies are given relative to the E_{tot} of the most stable α-ThC_2 polymorph.

(1) In agreement with experiments [3], our total energy calculations show that the most stable polymorph is monoclinic α-ThC_2, whereas β-ThC_2 is intermediate and cubic γ-ThC_2 is the most unstable polymorph and presumably can be stabilizing at high temperatures by the entropy factor. In order to estimate the relative stability of ThC_2 polymorphs, their Gibbs free energies ($G = E^o + P{\cdot}V{-}T{\cdot}S$) should be obtained. Since all our calculations are performed at zero temperature and zero pressure conditions, the *G* becomes equal to the E^o and, for example, for comparative estimation of stability of α and β polymorphs the value of $\Delta E_{tot} = \{E_{tot}(\alpha\text{-}ThC_2) - E_{tot}(\beta\text{-}ThC_2)\}$ may be used. In this way, we have obtained $\Delta E_{tot} = 0.063$ eV/form.unit (6.08 kJ/mol) for α-$ThC_2 \leftrightarrow \beta$-$ThC_2$ transition and $\Delta E_{tot} = 1.707$ eV/form.unit (164.72 kJ/mol) for β-$ThC_2 \leftrightarrow \gamma$-$ThC_2$ transition. In the experiments, the enthalpy for α-$ThC_2 \leftrightarrow \beta$-$ThC_2$ and β-$ThC_2 \leftrightarrow \gamma$-$ThC_2$ transitions are estimated at about 2.1 and 10.5 kJ/mol, respectively [3]. Naturally, the thermodynamic factors such as temperature and pressure should be taken into account at such comparisons.

Table 1

Calculated total energies (E_{tot}, eV per ThC_2 molecule), atomic positions, lattice constants (*a*, *b* and *c*, in Å), *d*(C–C) distances (for C_2 dumbbells, in Å), and theoretical density (ρ, in g/cm^3) for ThC_2 polymorphs in comparison with available experimental data.

Polymorph/parameter	α-ThC_2	β-ThC_2	γ-ThC_2
*E*tot*	0.000	0.063	1.770
a	6.6283 (6.692 [5] 6.684 [6])**	3.8069 (4.221 [5] 4.235 [20])	5.8097 (5.806 [5] 5.807 [20])
b	4.2069 (4.223 [5] 4.220 [6])	–	–
c	6.6726 (6.744 [5] 6.735 [6])	6.3826 (5.395 [5] 5.408 [20])	–
Wyckoff positions for Th	4(*e*) 0; 0.1990; ¼ (0; 0.2074; ¼) [5] (0; 0.2022; ¼) [6]	2(*a*) 0; 0; 0	4(*a*) 0; 0; 0
Wyckoff positions for carbon	8(*f*) 0.3006; 0.1356; 0.0523 (0.2992; 0.1326; 0.0540) [5]; (0.2986; 0.1305; 0.0513) [6]	4(*e*) 0; 0; 0.3957 (0; 0; ½ [5,18] – for dimer C_2)	4(*b*) 0; 0 ; 0.3375 (½; ½; ½ [5,20] – for dimer C_2)
d(C-C)	1.328	1.331	1.326
ρ	9.03 (9.14 [3])***	9.15	8.64 (9.00 [3])

* With respect to the E_{tot} of α-ThC_2.

** Available experimental data are given in parentheses.

*** For composition α-$ThC_{1.94}$ [3].

(2) The calculated structural parameters for all ThC_2 polymorphs are summarized in Table 1. As can be seen, for α and γ polymorphs our results are very similar to experiments. On the other hand, for tetragonal β-ThC_2 our calculations have overestimated the parameter *c* ($c^{theor} = 6.3826$ Å *versus* $c^{exp} = 5.395 - 5.408$ Å [5,20]) whereas, the parameter *a* is underestimated ($a^{theor} = 3.8069$ Å *versus* $a^{exp} = 4.221 - 4.235$ Å [5,20]). This result presumably may be explained taking into account the partial thermal disorientation for C_2 dumbbells (for example, the orientation of a part of the C_2 dumbbells in the plane perpendicular to the *c* axis, see Ref. [3]) – in comparison with ideal ordering of C_2 dumbbells along *c* axis, as it was postulated in our model. Besides it is necessary to take into account the non-stoichiometry effect: the tetragonal β-ThC_2 has a homogeneity range between C/Th = 1.66 and 1.94 [3].

(3) The bulk moduli (*B*) and its pressure derivative (*B*′), derived from the fit to Murnaghan's equation of state, as well as compressibility ($\beta = 1/B$), are given in Table 2. From these data, we see that the maximal and minimal values of the bulk moduli adopt β-ThC_2 and γ-ThC_2; whereas the compressibility of ThC_2 polymorphs changes in the inverse sequence. A simple explanation of these data follows from the known correlation between the bulk moduli *B* and cell volumes *V* ($B \sim V^{-k}$ [21]), see Table 2. Thus, among all ThC_2 polymorphs, γ-ThC_2 adopts the minimal *B* and maximal compressibility; *i.e.* in comparison with other ThC_2 polymorphs, γ-ThC_2 is the most soft material. Finally, the comparison of our data (Table 2) with the same for cubic ThC monocarbide [3,8,10] demonstrate that $B(ThC_2) > B(ThC)$. Thus, based on the well-known correlations between the bulk moduli and mechanical strength [22], we conclude that with growth of carbon content (*i.e.* as going from ThC to ThC_2) the hardening of a material occur. This conclusion agree with Vickers hardness measurements for ThC_z samples with the variable Th/C content ($1 < z < 2$), see [3].

3.2. Energies of formation

To provide the further insight of the fundamental aspects of phase equilibrium in the Th–C system, we have performed the estimations of the formation energies for ThC_2 polymorphs. For this purpose, the total energies of ThC_2 and its constituents in formal reactions $ThC_2 = Th + 2C^g$ or $ThC_2 = ThC + C^g$ are calculated, and the formation energies (E_f) of ThC_2 polymorphs are defined as:

$$E_f(ThC_2) = E_{tot}(ThC_2) - \{E_{tot}(Th) + 2E_{tot}(C^g)\} \quad (1)$$

$$E_f(ThC_2) = E_{tot}(ThC_2) - \{E_{tot}(ThC) + E_{tot}(C^g)\} \quad (2)$$

where E_{tot} are the total energies of ThC_2 polymorphs, cubic ThC, metallic thorium (α-Th), and graphite (C^g) at their optimized geometries as calculated in the same VASP approach. In this way, negative values of E_f point out the formation of stable dicarbide polymorphs, but their formation will be unlikely at the ordinary conditions if $E_f > 0$. Certainly, this prediction is based only on the thermodynamics and does not take into account the kinetics of reactions.

Table 2
Calculated bulk moduli (*B*, in GPa), their energy derivatives (*B*′), compressibility (*β*, in 1/GPa), and cell volumes (*V*, in Å^3) for ThC_2 polymorphs.

Polymorph/parameter	α-ThC_2	β-ThC_2	γ-ThC_2
B	129.1	149.2	121.6
B′	3.84	4.13	3.71
β	0.00775	0.00670	0.00822
V	46.92	46.28	49.02

Formation energies calculated for the different reactions are shown in Table 3 and allow us to make the following conclusions.

(1) For α and β polymorphs, we obtained, that their formation from the simple reagents (α-Th and C^g) as well as from ThC and carbon is favorable – against γ polymorph, for which the formation energy was obtained as positive.

(2) For both reactions (1) and (2), we have obtained, that the negative values of E_f for α polymorph are higher than for β polymorph; this means that the stability of α-ThC_2 is higher – in accordance with the thermodynamic data [3].

(3) Synthesis of ThC_2 with the participation of ThC as a reagent is the most energetically unfavorable, and this fact can be explained by the high stability of thorium monocarbide [3,10].

3.3. Electronic properties

In order to gain a deeper insight of the comparative peculiarities of the electronic properties of ThC_2, the calculations of their electronic structures have been performed. Total densities of states (DOS) for all ThC_2 polymorphs, depicted in Fig. 3, contain three main bands (A–C). The most significant differences for ThC_2 polymorphs are the width of the occupied valence bands (~7.6 eV for β-, ~8.6 eV for γ- and ~7.3 eV for α-polymorph) and the presence of the gap (~0.4 eV) between A and B bands for monoclinic α-ThC_2 *versus* the continuous character of spectra for the others polymorphs.

The total density of states at the Fermi level $N(E_F)$ adopts the non-zero value (*i.e.* all polymorphs have a metallic conductivity) and the minimal value of $N(E_F)$ is for the most stable monoclinic α-polymorph, Table 4.

The above calculations allow us to estimate for ThC_2 polymorphs the specific heat coefficient (γ) and the Pauli paramagnetic susceptibility (χ), assuming the free electron model, as: $\gamma = (\pi^2/3)N(E_F)k_B^2$, and $\chi = \mu_B^2 N(E_F)$; the results show the tendency

Table 3
Formation energies (E_f, eV/Th atom) for ThC_2 polymorphs for the different reactions.

Polymorph/reaction	α-ThC_2	β-ThC_2	γ-ThC_2
$ThC_2 = Th + 2C^g$	−0.92	−0.86	0.27
$ThC_2 = ThC + C^g$	−0.22	−0.16	0.97

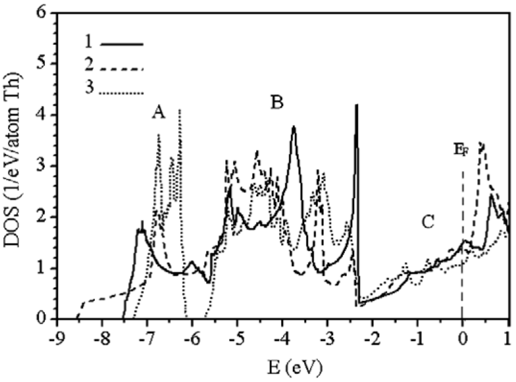

Fig. 3. Total densities of states for ThC_2 polymorphs: (1) tetragonal β-ThC_2; (2) cubic γ-ThC_2 and (3) monoclinic α-ThC_2.

of growth of γ and χ as going from α-ThC$_2$ to β,γ-ThC$_2$. Let us note also that the calculated specific heat coefficient (γ) for stable α-ThC$_2$ (2.614 mJ mol^{-1} K^{-2}) is higher than the same for cubic monocarbide ThC ($\gamma^{ThC} \sim 1.87$ mJ mol^{-1} K^{-2}) [8]; and this tendency agree with the available experiments: $\gamma^{ThC_2} = 3.13$ mJ mol^{-1} K^{-2} $> \gamma^{ThC} = 2.12 - 2.92$ mJ mol^{-1} K^{-2} [3].

3.4. Chemical bonding

Let us discuss the peculiarities of chemical bonding in thorium dicarbides. Further for the analysis of the hybridization effects (*i.e. the covalent bonding* character) the atomic-resolved *l*-projected DOS, and the charge density maps are employed. For the description of *ionic bonding* for ThC$_2$ we have made a Bader [23] analysis. In this approach each atom of a crystal is surrounded by an effective surface that runs through minima of the charge density, and the total charge of an atom (so-called Bader charge, Q^B) is determined by integration within this region.

Formally, one could consider ThC$_2$ crystal as Th^{4+}(C$_2$)$^{4-}$, where thorium is as four-electron donor. However, this simplified 'pure ionic' picture ignores the presence of covalent thorium–carbon bonding.

As can be seen from the Fig. 4, where on the example of β-ThC$_2$ polymorph the site-projected DOSs are depicted, there are significant hybridization effects of C 2*p* states with the Th (6*d* + 5*f*) states (in the interval from −7.6 up to −2.2 eV), which indicate the presence of the strong covalent Th–C bonding. Let us note also, that the Th–C bonds are formed not only along of the *c* axis (as a quasi-one-dimensional σ-like bonds ..Th–C–C–Th–C–C–Th..), but also 'lateral' π-like overlapping C$_2$–Th takes place, see Fig. 5. Here, it can be seen also that 'direct' Th–Th bonds are very small.

Table 4
Total densities of states at the Fermi level (N(E_F), in states/eV·atom Th), electronic heat capacity γ (in mJ K^{-2} mol^{-1}) and molar Pauli paramagnetic susceptibility χ (in 10^{-4} emu/mol) for ThC$_2$ polymorphs.

Polymorph/parameter	α-ThC$_2$	β-ThC$_2$	γ-ThC$_2$
N(E_F)	1.109	1.426	1.410
γ	2.614	3.361	3.324
χ	0.357	0.459	0.454

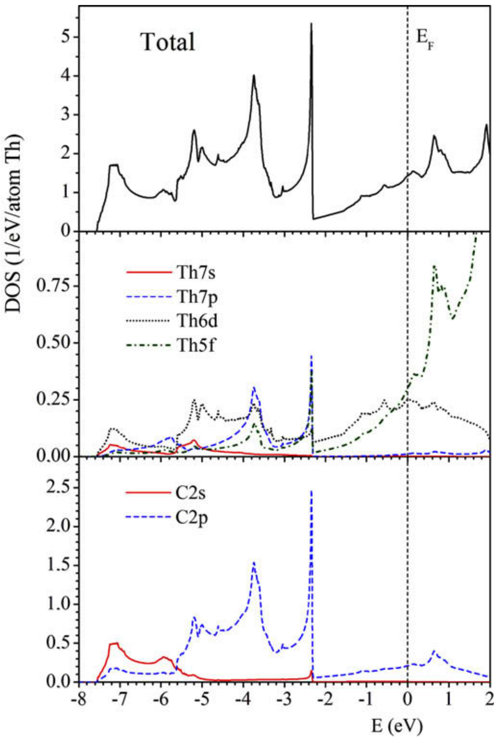

Fig. 4. Total (*upper panel*) and partial atomic-resolved densities of states for tetragonal β-ThC$_2$ polymorph.

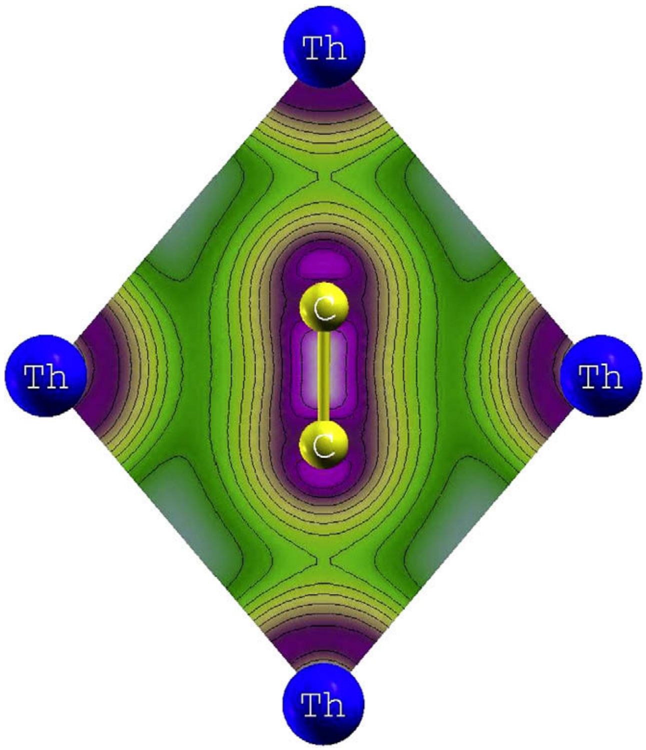

Fig. 5. Valence charge density map in (1 1 0) plane of β-ThC$_2$ polymorph.

Finally, our estimations of Bader charges show that the amounts of electrons redistributed between the Th atoms and C$_2$ dumbbells are far from those predicted in the idealized ionic model (4*e*); namely, the charge transfer ΔQ(Th → C$_2$) is about 1.95*e*.

4. Conclusions

In summary, the first-principles VASP-PAW with spin–orbit calculations have been performed for systematic study of structural, elastic, cohesive and electronic properties of all three polymorphs (α-monoclinic, β-tetragonal and γ-cubic) of thorium dicarbide ThC$_2$. The main conclusions are the following.

According to our calculations, among all ThC$_2$ polymorphs, high-temperature γ-ThC$_2$ with maximal cell volume and minimal density adopts the minimal *B* and maximal compressibility; *i.e.* in comparison with other ThC$_2$ polymorphs, γ-ThC$_2$ is the most soft material. We conclude also that with growth of carbon content (*i.e.* as going from ThC to α-ThC$_2$) the hardening of a material occur.

The estimations of the formation energies of ThC$_2$ polymorphs for different possible preparation routes (namely for the reactions with the participation of simple substances (metallic Th and graphite) or thorium monocarbide ThC and graphite) show that the synthesis of the ThC$_2$ polymorphs from simple substances is more favorable – in comparison with the reactions with participation of Th monocarbide.

The present results indicate that the electronic spectra of all ThC$_2$ polymorphs are similar, with non-zero value of the density of states at the Fermi level, *i.e.* all these materials have a metallic conductivity. The minimal value of N(E_F) is for the most stable monoclinic α polymorph. Our analysis reveals that bonding in ThC_2 polymorphs is of a mixed covalent–ionic–metallic character. Namely, the covalent bonding is formed due to hybridization effects of C–C states (for C_2 dumbbells) and C_2–Th states. In addition, between the thorium atoms and C_2 dumbbells, ionic bonds emerge owing to the charge transfer Th → C_2. Note that the amounts of electrons redistributed between the Th atoms and C_2 dumbbells (at about 1.95*e*) are much less than assumed in the idealized ionic model (4*e*). The metallic-like Th–Th bonds are formed by near-Fermi delocalized Th *d,f* states.

Finally, our analysis was performed for stoichiometric ThC_2 polymorphs with idealized crystal structures. As an important issue for future studies, the great interest is the presence of the lattice vacancies (*i.e.* the effect of the carbon non-stoichiometry) as well as the partial disorientation of the C_2 dumbbells and their comparative influence on the properties of ThC_2 polymorphs.

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