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Mechanical stability and superconductivity of PbO-type phase of thorium monocarbide at high pressure

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ABSTRACT

As a potential nuclear fuel for the next generation of nuclear reactors, the structural and physical properties of thorium monocarbide (ThC) under high pressure have attracted a wide range of research interest. Here, the mechanical, electronic, dynamical, and superconducting properties of PbO-type ThC have been systematically investigated through first-principles calculations, which established the thermodynamic and mechanical stability of this phase within the pressure range of 60–140 GPa. Moreover, it is found that pressure significantly affected the electronic states near the Fermi level and superconductivity. The superconducting transition temperature T_c first increases, and then decreases with increasing pressure. The maximal value of T_c reaches 4.64 K at 80 GPa. This phenomenon is a representation of the reconstruction of the Fermi surface and phonon hardening under compression.

1. Introduction

Research on actinide carbides began in the 1950s; recently, there has been renewed interest in actinide carbides, such as thorium carbides, for the purpose of potential nuclear fuels for fast nuclear reactors with closed fuel cycles [1–4]. Compared with existing uranium-based nuclear fuels, thorium-based fuels have many excellent physical properties such as, for example, lower thermal expansion coefficients, higher corrosion resistivity, higher melting points, and larger thermal conductivity [5–9]. Owing to the prospective application of thorium carbides as outstanding fuel materials, it is very important to understand their structures and physical properties in order to model the fuel behavior at high pressures/temperatures. Despite the abundant research on actinide compounds, such as Th [10–12], ThN [13], ThC_2 [14], and ThO_2 [15], however, for ThC, we only know that thorium monocarbide has a B1 structure at ambient conditions. The structural, thermodynamic, electronic, and elastic properties of this structure have been studied by many research groups [16–26]. However, the high-pressure properties of ThC, to the authors' knowledge, are not well known from experimental or theoretical investigations. Meanwhile, due to the discovery of the High-Tc of ~203 K of H-S system at high pressure [27], the field of conventional superconductivity under pressure get particular attention recently. This significant finding is originally achieved by a theoretical prediction [28].

Motivated by these observations, in this paper, we systematically study the electronic, mechanical, kinetic, and superconductivity properties of a new high-pressure PbO-type phase [29,30] of thorium monocarbide (space group $P4/nmm$) within the pressure range of 60–140 GPa.

2. Computational methods

Ab initio calculations were carried out using the density functional theory (DFT) [31,32] as implemented in the Quantum-ESPRESSO package [33]. The generalized gradient approximation (GGA) exchange correlation function of Perdew–Burke–Ernzerhof (PBE) was utilized [34]. The thorium $6s^26p^66d^27s^2$ and carbon $2s^22p^2$ were treated as valence electrons. A cut-off energy of 100 Ry and $10 \times 10 \times 12$ Monkhorst–Pack [35] k-point meshes for the electronic Brillouin zone (BZ) sampling were employed, achieving a higher level of accuracy of total energy, within 0.01 mRy/atom. The phonon calculations were based on the density function linear-response method [36–42]. A higher level of accuracy with $26 \times 26 \times 32$ k-grid and Gaussians smearing 0.03 Ry was used to achieve phonon modes converged within 0.001 THz. Meanwhile, a $3 \times 3 \times 4$ q-points grid in the first BZ was adopted as the interpolation of the force constants about the phonon band calculation. The superconducting calculations employed a dense $15 \times 15 \times 18$ MP confirmed k-point grid

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convergence with Gaussians smearing 0.02 Ry, which essentially achieved the zero-width limit of electron–phonon interacting calculations [43–47]. However, the study on the accurate elastic constants and modulus are investigated within the Voigt–Reuss–Hill approximation [48] as actualized in the Vienna *ab initio* simulation package (VASP) [49].

3. Results & discussion

The PbO-type phase of of thorium monocarbide is a new high-pressure structure and exhibits metallic. Herein, the cell volume and atomic positions for the PbO-type ThC are full optimized at 58.3 GPa. The calculated equilibrium lattice constants *a*, *b* and *c* of this phase are in good agreement with experimental values within 2% (Table 1), supporting the choices of our pseudopotential and functional.

The elastic constants show the nature of the stability and mechanical properties of materials by analyzing the behavior of objects under the elastic deformations. Six independent elastic constants, C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66} have been given in a tetragonal structure. In this work, the corresponding elastic constants were acquired by the slopes of the acoustic phonon modes within the long-wave limit, as seen in Fig. 1a. It shows the pressure dependence of the elastic constants of the PbO-type tetragonal structure of ThC. We can see that the independent modes C_{11}, C_{12}, C_{33}, C_{44}, and C_{66} are monotonously enhanced with increasing pressure. Only the elastic constant C_{13} first decreases and then increases with increasing pressure. However, all the elastic constants are always positive in our pressure range. This indicates that the structural phase transition does not occur. The bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio *v* were studied using the Voigt–Reuss–Hill averaging approximation. The physical quantities *E* and *v* are related to *B* and *G*. Fig. 1b shows the quantities *B*, *G*, and *E* under different pressures, which also increase linearly with pressure. Furthermore, our elastic constants are in accordance with the mechanical stability criteria [50] for the tetragonal symmetry under compression, namely.

$$C_{11} > 0, C_{33} > 0 C_{44} > 0, C_{66} > 0, (C_{11} - C_{12}) > 0,$$
$$(C_{11} + C_{33} - 2C_{13}) > 0, (2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0$$

This further supports our calculated results.

Fig. 2 shows the calculated band structures at 60, 100, and 140 GPa. As seen in the figure, we observed two electronic bands crossing the Fermi level (E_F) along the M–Γ–Z and X–Γ directions at 60 and 100 GPa. When the pressure increases to 140 GPa, the four electron bands pass along the same line through the Fermi level. Moreover, it is found that electronic band just touching E_F at the *Z* point crosses it with pressure. The electronic bands near the *M* and *X* points also pass through E_F under compression. Meanwhile, owing to the observable electronic states near the Fermi surface, ThC exhibits obvious metallic behavior. Since the parabolic conduction and valence bands are less dispersed near the Fermi level, it will support superconducting behavior.

Furthermore, the electron states of the Fermi surface can play a role in the ordinary transport properties of the metallic system. In the simple condition, the Fermi surface would be a sphere, the radius of which is shown by the Fermi wave vector. Obviously, the Fermi surface of this phase deviates from the spherical shape.

Table 1
Lattice constants of PbO-type ThC at 58.3 GPa obtained from here and experiment.

Space group	Method	*a* (Å)	*c* (Å)	Ref.
*P*4/nmm	PWSCF-PBE	4.128	3.063	This work
	Expt. data	4.205	3.099	[30]

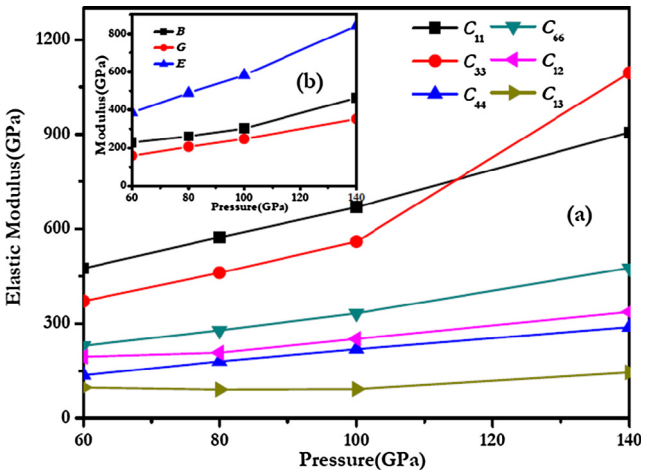

Fig. 1. (a) Pressure dependence of the elastic constants in PbO-type ThC. (b) Bulk modulus *B*, shear modulus *G*, and Young's modulus *E* for ThC as functions of pressure.

In particular, such a case has been encountered in the multivalent states for metals. When depicted in an extended BZ, the Fermi surface associated with the lowest conduction band appears as some changes near the *Z*, *M*, and, *X* points with pressure. Supposing that electrons very close to the Fermi energy level make a main contribution to superconductivity, in many instances, the shape of the Fermi surface with respect to the BZ becomes a guide to studying the electrical properties of the metal. The Fermi surface of new phase of ThC (Fig. 3(a) and (b)) coincide with two energy bands crossing the Fermi level (Fig. 2(a) and (b)). As shown in Fig. 3, the center of all of the Fermi surfaces is located in the Γ point under different compressions, while the Fermi surface undergoes reconstruction under compression. The Fermi surface of PbO-type ThC (Fig. 3(c)) corresponds with four bands crossing the Fermi level (Fig. 2(c)). In general, if the shape of the Fermi surface changes abruptly, the Van Hove singularity appears in the state, enhanced T_c. However, as will be discussed later, the T_c value of ThC decreases with the increase in pressure (Table 2).

Next, we still study the dynamic stability of the PbO-type phase of ThC under compression. No imaginary phonon frequencies are observed in the whole BZ, indicating the dynamic stability of this structure in a wide pressure range. Fig. 4 shows the calculated phonon dispersion relation and the state of the projected phonon density in the tetragonal structure of ThC at 140 GPa. It is indicated that this PbO-type tetragonal phase is an approved structure for thorium monocarbide at high pressures, even to 140 GPa. Owing to the fact that the atomic mass of the thorium atom is much higher than that of the carbon atom, the phonon dispersion relations obviously divide into two portions with a wide gap: one portion is the range between 0 and 8.3 THz, where the contribution of thorium atoms is dominant; the other portion is in the domain of 16.5–25 THz, where the phonon vibration frequencies are mainly from carbon atoms.

Subsequently, we further calculate the phonon spectrum, Eliashberg spectral function $\alpha^2F(\omega)$, and the electron–phonon coupling (EPC) constant λ for PbO-type ThC to probe its possible superconductivity in Fig. 4. The lack of any imaginary phonon modes indicates lattice dynamical stability of the structure in our pressure range, as shown in Fig. 4(a). A wide gap separates the phonon dispersive curve into two parts. The lower vibration modes are mainly related to the motions of Th atoms; However, the higher frequency modes are related to C atoms. The common contribution (nearly 71.2 and 28.8%, respectively) gives a λ value of 0.418 with the pressure up to 140 GPa. Moreover, it is found that there are some