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Mechanical stability and thermodynamic properties of OsC from first-principles calculations

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ABSTRACT

The elastic and thermodynamic characteristics of OsC crystal have been predicted through a method of density functional theory within the generalized gradient approximation (GGA). Compared with WC-type OsC, NaCl-type OsC is not only energy unfavorable but also mechanics unstable. The five independent elastic constants (C_{ij}), bulk modulus (B_0), the dependence of bulk modulus on temperature and pressure as well as the thermal expansion coefficient (α_V) at various temperatures for WC-type OsC are discussed. According to our calculations, WC-type OsC should be an ultra-incompressible material with high bulk modulus about 381 GPa. In addition, the bulk modulus will increase with increasing pressure while decrease with increasing temperature. The researches on the thermal expansion coefficient indicate that there will be a knee point during the process of thermal expansion coefficient variation versus increasing temperature. Our results may provide useful information for theoretical and experimental investigation of OsC.

1. Introduction

Many attentions have been paid to transition metal carbides. Not only do they spur the fundamental scientific challenge of finding methods to control, tune and enhance their peculiar physical properties, but they also have important technical applications such as cutting tools, super-abrasive materials and wear-resistant coatings [1]. According to theoretical and experimental researches, one important conclusion has been deduced: ultra-incompressible and ultra-hard materials may be synthesized by combining a high valence electron density transition metal with a small main group elements (B, C, N)[1–4]. More recently, Hsiu-Ying Chung et al. [4] have synthesized ultra-incompressible material of ReB_2 by this method. According to this theory, transition metal carbides should be also potential ultra-incompressible materials. Recently, Huiyang Gou et al. [5] have studied MC (M = W, Os, Ir, Re) and found these transition metal carbides should possess excellent mechanical properties. Jin-Cheng Zheng [6] has investigated OsC with NaCl-type and WC-type structures and pointed out that WC-type OsC should be much more favorable in energy. But for OsC crystal, which structure is the stable one? Such a primary problem is still inconclusive until now.

Though some researches have been done on OsC, most of them are focused on electronic structure and property; few pay attention to the elastic and thermodynamic properties under high temperature and pressure. In this study, we will use the first-principles methods to study the mechanical stability for both cubic and hexagonal OsC. In addition, the elastic and thermodynamic properties of hexagonal OsC are also investigated by using a quasi-harmonic Debye model. Our results will provide useful information for further researches of OsC crystal.

2. Methods

The calculations are based on the density functional theory (DFT) [6] within the generalized gradient approximation (GGA) [7] using ultra-soft pseudo-potential and plane wave basis sets [8,9] implemented in the VASP code. The plane wave cut-off is 400 eV for structural optimization and 470 eV for static electronic structural calculation. Brillouin zone sampling is preformed on a grid of $21 \times 21 \times 21$ Monkhorst-Pack special points and the self-consistent convergence of the total energy is at 1×10^{-6} eV/Atom. The lattice vectors and atomic coordinates of OsC are relaxed at a series of fixed volumes by optimizing both the forces and stresses.

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The residual force and stress in the equilibrium geometry are of the order of 0.01 eV/Å and 10^{-3} GPa, respectively. The obtained energies are fitted to the third-order Birch-Murnaghan equation of state (EOS) [10] to give the equilibrium volume and energy.

3. Results and discussion

OsC may be in hexagonal WC-type structure with space group P-6m2(*No.*187) and cubic NaCl-type structure with space group Fm-3m (*No.* 235) [5–6]. The present calculated equilibrium lattice parameters are $a = 2.952$ Å and $c = 2.728$ Å for WC-type and $a = 2.182$ for NaCl-type OsC, which agree well with the other theoretical and experimental results [11,12], as shown in Table 1. In addition, we have also calculated the equilibrium volumes and energies for both the two types of crystal, which are also listed in Table 1. It can be seen that the WC-type OsC has much smaller cell volume and lower total energy, which are in line well with the other result [6] and indicate that WC-type OsC is much more energy favorable.

In order to calculate elastic constants of a crystal, some defined strains should be loaded to the unit cell. Because the internal energy $E(V, \{\delta_i\})$ of the strained crystal can be expanded in series with respect to the corresponding strain (δ_i) and the equation with a Voigt notation can be expressed as follows:

$$E(V, \delta_i) = E(V, 0) + V \sum_{i=1}^{6} \sigma_i \delta_i + \frac{1}{2} V \sum_{i,j=1}^{6} C_{ij} \delta_i \delta_j + \ldots \quad (1)$$

where V is the equilibrium cell volume; $E(V,0)$ and $E(V,\delta_i)$ are the ground state and corresponding strained crystal energy. σ_i and δ_i denote the stress tensor and strain tensor respectively. C_{ij} denotes the elastic constant.

For hexagonal crystal, there are five independent elastic coefficients (Named C_{11}, C_{12}, C_{13}, C_{33} and C_{44}), which can be determined by five sets of strains. And for cubic crystal, there are only three independent elastic coefficients (named C_{11}, C_{12} and C_{44}). We carry out calculations for eight values of strain from −0.012 to 0.012 in step of 0.003. The energy of the stained crystal can be determined by using the first-principle calculation easily and the elastic constants can be deduced by fitting the corresponding two-order polynomial of $E(\delta_i)$ and δ_i. The present results and other available results are listed in Table 2. Unfortunately, there are still no available experimental elastic constants of OsC and only some theoretical results are available. The five independent elastic constants for WC-type OsC are: $C_{11} = 430$ GPa, $C_{12} = 386$ GPa, $C_{13} = 346$ GPa, $C_{33} = 433$ GPa and $C_{44} = 79$ GPa, and the three independent elastic constants for NaCl-type OsC are: $C_{11} = 510$ GPa, $C_{12} = 272$ GPa and $C_{44} = -90$ GPa, as shown in Table 2.

For a stable hexagonal structure, the five independent elastic constants (C_{11}, C_{12}, C_{13}, C_{33} and C_{44}) should be satisfied with the well-known Born-Huang criteria [13] as follows:

$$C_{11} - C_{12} > 0, C_{12} > 0, C_{33} > 0, C_{44} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \quad (2)$$

while for a stable cubic crystal, the three independent elastic constants (C_{11}, C_{12} and C_{44}) should be satisfied with [13] in-equations as follows:

$$C_{11} > 0, C_{44} > 0, C_{11} > |C_{12}|, C_{11} + 2C_{12} > 0 \quad (3)$$

Obviously, for NaCl-type OsC, it is mechanics unstable because of the $C_{44} < 0$, and for WC-type OsC, the elastic constants are satisfied with the Born-Huang criteria, which indicates that WC-type is mechanically stable. Therefore, we only discuss the elastic and thermodynamic properties of hexagonal OsC in the following parts.

In order to obtain the macroscopic mechanical parameters of WC-type OsC, we have calculated the bulk modulus and shear modulus in the Voigt methods [11], the formulas are listed as follows:

$$B_V = \frac{2}{9}\left(C_{11} + C_{12} + \frac{C_{33}}{2} + 2C_{13}\right) \quad (4)$$

$$G_V = \frac{1}{15}(C_{11} + C_{33} - 2C_{13} + 6C_{44} + 5C_{66}) \quad (5)$$

And the results are listed in Table 2. Where the $C_{66} = 1/2(C_{11} - C_{12})$. According to our calculation, the bulk modulus deduced from the elastic constants is 383 GPa at $T = 0$ K and $P = 0$ GPa which is in agreement well with the one about 381 GPa obtained through fitting the three-order Brich Murnaghan equation of state. The Young's Modulus [14] (E) and the anisotropic factor [15] (A) can be obtained from the formulas

Table 1
The present and other results about the lattice constants a and c, the cell total energy E as well as the equilibrium cell volume V of OsC with WC-type and NaCl-type structure.

Crystal type		Lattice constants (Å)		Volume (Å^3)	Energy(eV)
		a	c	V	E
WC-type	This work	2.953	2.729	20.610	−18.5447
	Experi. [11]	2.908	2.821	–	–
	Otherother cal. [6]	2.928	2.717	20.172	–
NaCl-type	This work	4.363	–	20.770	−17.621
	other cal. [6]	4.333	–	20.352	–

Table 2
The calculated elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), the young's modulus (E) and anisotropic factor (A) of OsC with WC-type and NaCl-type structure respectively.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	E	A
WC-type	430	386	346	433	79	383	50	144	3.791
NaCl-type	510	272	–	–	−90	–	–	–	–

The A is a dimensionless parameter and the others are in unit of GPa.