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Pressure-induced structural phase transition, elastic and thermodynamic properties of ReC under high pressure

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ABSTRACT

The pressure-induced structural phase transition of rhenium monocarbon (ReC) is investigated via the projector augmented wave (PAW) method with the generalized gradient approximation (GGA). Using the first-principles calculations, the equilibrium structural parameters of ReC in rocksalt (NaCl), cesium chloride (CsCl), zinc blende (ZB), wurtzite (WZ), nickel arsenide (NiAs) and tungsten carbide (WC) types are successfully obtained, and the results are well consistent with other theoretical data. It is firstly noted that WC-ReC translates into CsCl-ReC at 510.50 GPa by analyzing the enthalpy difference versus pressure. From the calculated elastic constants, the aggregate elastic modulus (B, G, E), the Poisson's ratio (σ) and the Debye temperature Θ_D of WC-type are also derived. It is observed that all the data of WC-ReC obtained increase monotonically with increasing pressure. Meanwhile, the thermodynamic properties of WC-ReC under high temperature and high pressure are investigated applying nonempirical Debye model in the quasi-harmonic approximation.

1. Introduction

The superhard materials (SHM), whose Vickers hardness exceeds 40 GPa, have been widely used in industrial applications [1], such as cutting and polishing tools, abrasive materials, wear-resistant coatings and diffusion barriers [2–5]. Rhenium Carbon, as a 5d transition metal monocarbides which has an unusual mixture of covalent, metallic, and ionic bonds, possesses excellent properties, as high hardness, high melting points and good corrosion resistance [3]. Hence, it has triggered great interest to physical scientists.

Experimentally, in 1975, S.V. Popova [6] obtained rhenium carbon in NaCl-type ($a = 4.005$ Å, $T_c = 3.4$ K) at high pressure and temperature. Theoretically, in 2007, Chen et al. [7] studied the electronic and mechanical of ReC in NaCl, ZB, NiAs, WC structures using Vanderbilt ultrasoft pseudopotential within generalized gradient approximation (GGA) and found that WC-type structure is energetically the most stable with the NiAs-type close in enthalpy as a metastable phase, and the results are also obtained by Zhao et al. [2] in 2009. In addition, Gou et al. [4] also obtained the same conclusion and calculated the hardness of ReC in WC-type under ambient condition. However, few reports have been made to the structural phase translation of ReC at zero temperature and many properties of ReC at high pressure have also hardly been studied.

Therefore, in this paper, we aim to research the structural phase transition, elastic and thermodynamic properties of ReC under high pressure by first-principle calculations. The rest of the paper is organized as follows: In section 2, we make a brief review of the calculation method. The results compared with the previous experimental and theoretical data are demonstrated in section 3. Our main conclusions are summarized in section 4.

2. Theoretical methods

2.1. Total energy electronic structure calculations

Our structural prediction is based on the Crystal structure AnaLYsis by Particle Swarm Optimization methodology (CALYPSO program). Local optimizations using Vienna *ab initio* simulation package (VASP code) [8], were done with the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1 × 10^{-5} eV per cell. After processing the first

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generation structures, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO and 40% of the structures in the new generation are randomly generated. The detailed method can be found in Refs. [9,10].

The electronic total energy calculations are performed within the density functional theory as implemented in the VASP. The exchange-correlation functional is treated by generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE). In the projector augmented wave (PAW) [11,12] method we used, the pseudopotentials for calculations are constructed by the electron configurations as Re $5d^56s^2$ and C $2s^22p^2$, and the accurate total energy calculations are conducted by the linear tetrahedron method with Blöchl [13] corrections. All the calculations have the same plane-wave cutoff energies of 650 eV. The Monkhorst-Pack [14] k-points are 21 × 21 × 21 for the cubic (NaCl, CsCl, ZB) structures and 19 × 19 × 15 for the hexagonal WZ and NiAs structures and 19 × 19 × 17 for WC structure. All the parameters are tested to be fully converged with respect to total energy and are sufficient to give good results. The total energy self-consistent convergence precision is set to 1×10^{-6} eV/cell.

2.2. Elastic constants

As is well-known, for a system with a small strain γ to the lattice primitive cell volume V, we can get the elastic constants by means of Taylor expansion of the total energy $E(V, \gamma)$. The internal energy of a strained system is expanded as follows [15,16]:

$$E(V,\gamma) = E(V_0,0) + V_0\sum_{i=1}^{6}\sigma_i\gamma_i + \frac{V_0}{2}\sum_{i,j=1}^{6}C_{ij}\gamma_i\gamma_j + \ldots \tag{1}$$

where $E(V_0, 0)$ is the total energy of the unstrained equilibrium volume V_0 under different pressures, σ is a factor present to take care of the Voigt index [15]. The method we applied is as below:

Considering a crystal compressed by the isotropic pressure P to the density $\rho_1 = 1/V_1$, there leads to be a homogeneous deformation in the strained lattice. Then the strained Bravais lattice point $\vec{R}'$ has been

$$\vec{R}'_i = \sum(\delta_{ij} + \varepsilon_{ij})\vec{R}_j \tag{2}$$

For a homogeneous strain, the parameter δ_{ij} is the Kronecher delta, ε_{ij} are simple constants, independent of $\vec{R}$, with $\varepsilon_{ij} = \varepsilon_{ji}$, where the subscripts i and j indicate the Cartesian components.

Originally, the fourth-rank tensor C has 21 independent components. For a hexagonal crystal, however, the number is reduced to five independent components C_{11}, C_{12}, C_{13}, C_{33} and C_{44} when taking into account the symmetry. The relationship between the strains and elastic constants is labeled in Table 1. The strains are non-volume-conserving. By applying appropriate deformation for the optimized unit cell, we have obtained the total energies E for the strained crystal structure. Then the calculated E-γ points are fitted to the fourth-order polynomials $E(V, \gamma)$ to give the elastic stiffness coefficients.

Table 1
The strains used to calculate the elastic constants of hexagonal WC-ReC.

	Strains	Distortion	$\rho_1\frac{\partial^2 E(\rho_1,\gamma)}{\partial\gamma^2}\Big\vert_{\gamma=0}$
Hexagonal	1	$\varepsilon_{11} = \varepsilon_{33} = \gamma$	$C_{11} + 2C_{13} + C_{33} - 2P$
	2	$\varepsilon_{11} = -\varepsilon_{22} = \gamma$	$2(C_{11} - C_{12} - P)$
	3	$\varepsilon_{11} = \varepsilon_{22} = \gamma$	$2(C_{11} + C_{12} - P)$
	4	$\varepsilon_{13} = \varepsilon_{31} = \gamma$	$4C_{44} - 2P$
	5	$\varepsilon_{33} = \gamma$	$C_{33} - P$

2.3. Thermodynamic properties

The quasi-harmonic Debye model [17] in which the phononic effects are considered, has been successfully investigated the thermodynamic properties of TiC [18], TcC [19]. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function G take the following form:

$$G = E + PV - A_{vib}(\Theta;T) \tag{3}$$

where E is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, and A_{vib} is the vibrational Helmholtz free energy, which can be written as [20].

$$A_{vib}(\Theta;T) = nKT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln\left(1 - e^{-\Theta/T}\right) - D\left(\frac{\Theta}{T}\right)\right] \tag{4}$$

where Θ, $D(\Theta/T)$, n represent the Debye temperature, the Debye integral and the number of atoms per formula unit, respectively. The non-equilibrium Gibbs function G, as a function of $(V; P, T)$, can be minimized with respect to volume V

$$\left(\frac{\partial G}{\partial V}\right)_{P,T} = 0 \tag{5}$$

By solving the thermal equations of states, we can obtain the isochoric heat capacity C_{V} and thermal coefficient α by the following formulas:

$$C_V = 3n\kappa\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{e^{\Theta/T} - 1}\right] \tag{6}$$

$$\alpha = \frac{\gamma C_V}{B_T V} \tag{7}$$

where γ is the Grüneisen parameter and B_{T} is the adiabatic bulk modulus, which are defined as

$$\gamma = -\frac{\gamma d(\ln\Theta(V))}{d(\ln(V))} \tag{8}$$

$$B_T = V\left(\frac{\partial^2 G}{\partial^2 V}\right)_{P,T} \tag{9}$$

3. Results and discussion

3.1. Pressure-induced structural phase transition

To obtain the equilibrium structural parameters, we select a wide range of volumes around the optimized reference values for the cubic NaCl, CsCl, ZB structures and hexagonal WZ, NiAs, WC structures at $P = 0$ GPa and $T = 0$ K, respectively. And then the corresponding total energies are obtained using PAW method within the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA). The calculated total energies are plotted as a function of volume in Fig. 1. It is noted from Fig. 1 that WC has the lowest energy (−21.24 eV/cell) at its equilibrium volume, which indicates the stability at ambient conditions.

By fitting the calculated energy-volume (E-V) to the third-order Birch-Murnaghan equation of state [21], we can determine the lattice parameters a, equilibrium volume V_0, bulk modulus B_0, and