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Electronic and thermodynamic properties of ReB_2 under high pressure and temperature

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ABSTRACT

First-principles calculations of the crystal structures of rhenium diboride (ReB_2) have been carried out with the plane-wave pseudopotential density functional theory method. The calculated values are in very good agreement with experimental data as well as with some of the existing model calculations. The quasi-harmonic Debye model, using a set of total energy versus molar volume obtained with the first-principles calculations, is applied to the study of the thermal and vibrational effects. The structural parameters, thermal expansions, heat capacities, Grüneisen parameters and Debye temperatures dependence on the temperature and pressure are obtained in the whole pressure range from 0 to 70 GPa and temperature range from 0 to 2000 K as well as compared with available data.

1. Introduction

Superhard materials have attracted considerable attention during recent years due to the importance in fundamental science and technological applications, such as cutting tools, high-temperature environments, and hard coating applications. Great effort is currently focused on the synthesis and characterization of superhard materials exhibiting simultaneously very low compressibilities, wide thermodynamic ranges of chemical stability, and high scratch resistance as well as surface durability [1–5]. Recently, it was found that ReB_2 can be synthesized at ambient pressure, and the result presented that ReB_2 crystal has super incompressibility along the c axis and high hardness comparable with diamond and cubic BN [6], respectively. Lately, the mechanical properties of ReB_2 were also correctly predicted by Hao et al. [7]. Further mechanical and electronic properties were studied by Liang et al. [8]. The electronic, elastic, phonon and thermal properties of ReB_2 have been investigated by first principle calculations [9–11].

Materials selection decisions for components that are exposed to elevated temperatures, temperature changes, and/or thermal gradients require the design engineer to have an understanding of the thermal responses of materials, as well as access to the thermodynamic properties of a wide variety of materials. Heat capacity, thermal expansion, and thermal conductivity are properties that are often critical in the practical utilization of solids. The Debye temperature is a fundamental parameter of a material which is linked to many physical properties such as specific heat, elastic constants, and melting point.

From the analysis above, we can see that the thermodynamic properties of ReB_2 under high pressures and temperatures are important and have never been studied in detail. So, we focus on it in this work.

2. Theory and calculated details

All calculations are performed based on the plane-wave pseudopotential density-function theory (DFT) [12]. Vanderbilt-type non-local ultrasoft pseudopotentials (USPP) [13] are employed to describe the electron–ion interactions. The effects of exchange–correlation interactions are treated with the generalized gradient approximation (GGA) of Wu–Cohen (WC) [14]. In the structure calculation, a plane wave basis set with energy cut-off 650.00 eV is used. Pseudo-atomic calculations are performed for B $2s^22p^1$ and Re $5s^25p^65d^56s^2$. For the Brillouin-zone sampling,

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Table 1

Lattice constants (Å), internal parameter, the axial ratio c/a, equilibrium volume (Å^3) and bulk modulus (GPa) of ReB_2 at zero pressure, compared with experimental and other theoretical data.

	a	c	c/a	u	V	B	B'
Our cal.	2.901	7.479	2.578	0.048	54.5328	346.29	4.24
Other cal.[a]	2.8809	7.4096	2.572		53.2613	354.5	
Other cal.[b]	2.8698	7.3946	2.577		52.7425	369.2	
Other cal.[c]	2.9007	7.4777	2.578	0.0478	54.502	350	
Other cal.[d]	2.872	7.405	2.578			359	4.09
Other cal.[e]	2.879	7.436	2.583			366	4.28
Other cal.[f]	2.913	7.506	2.577			341	4.0
Other cal.[g]	2.880	7.423	2.577		53.318	359.9	4.035
Exp.[h]	2.900	7.478	2.578	0.048	54.4643		
Exp.[i]					54.46	360	4.0

[a] Ref. [7]-GGA.
[b] Ref. [7]-LDA.
[c] Ref. [9].
[d] Ref. [8].
[e] Ref. [10]-LDA.
[f] Ref. [10]-GGA.
[g] Ref. [11].
[h] Ref. [25].
[i] Ref. [6].

the $13 \times 13 \times 5$ Monkhorst–Pack mesh [15] is adopted. The self-consistent convergence of the total energy is 10^{-7} eV/Atom and the maximum force on the atom is 10^{-4} eV/Å. All the total energy and electronic structure calculations are implemented through the CASTEP code [16,17].

In order to obtain the thermodynamic properties of ReB_2, the quasi-harmonic Debye model [18–21] is introduced, in which the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form of

$$G^*(V;P,T) = E(V) + PV + A_{Vib}(\Theta(V);T). \tag{1}$$

Here $E(V)$ is the total energy per unit cell for ReB_2, $\Theta(V)$ is the Debye temperature, and the vibrational Helmholtz free energy A_{Vib}can be written by [22,23]

$$A_{Vib}(\Theta;T) = nKT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-e^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right)\right]. \tag{2}$$

Here $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed as

$$\Theta = \frac{\hbar}{K}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}}. \tag{3}$$

Here M is the molecular mass per formula unit, B_s the adiabatic bulk modulus, the Poisson ratio σ is taken as 0.22 [10]. According to Refs. [22,24], $f(\sigma) = 0.918059$. For the compound ReB_2, $n = 3$, $M = 207.827$ a.u. Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V as follows:

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \tag{4}$$

By solving Eq. (4), the isothermal bulk modulus and other thermal properties such as heat capacity at constant volume C_V, the heat capacity at constant pressure C_P, and thermal expansion α are respectively taken as:

$$B_T(P,T) = -V\left(\frac{\partial P}{\partial V}\right) = V\left(\frac{\partial^2 G*(V;P,T)}{\partial V^2}\right)_{P,T}. \tag{5}$$

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

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

$$C_P = C_V\,(1+\alpha\gamma T) \tag{8}$$

where γ represents the Grüneisen parameter and it is expressed as $\gamma = -(\mathrm{d}\ln\Theta(V)/\mathrm{d}\ln V)$.

3. Results and discussion

3.1. The static equilibrium lattice structure

ReB_2 has a simple hexagonal structure (space group 6_3/mmc) with experimental $a = 2.900$ Å and $c = 7.478$ Å [25], the dependent structure parameters are the primitive cell volume V_0, the axial ratio c/a, and the internal parameter u. For the experimental ReB_2, the axial ratio $c/a = 2.579$, and the internal parameter $u = 0.048$. To determine the equilibrium geometry of the ReB_2, we perform the following procedures. In the first step, for a given u, the ratio c/a is fixed, which varies in the range from 2.560 to 2.598 with steps of 0.001, a series of different a and c are obtained to calculate the total energies, the minimum total energy is found for the given u. In the following step, we repeat the above step for several u, which varies in the range from 0.036 to 0.060 with steps of 0.001, and then find the minimum total energy for the each u, in order to obtain the most stable structure of the ReB_2, which corresponds to $a = 2.901$ Å, $c = 7.479$ Å, $u = 0.048$, and $c/a = 2.578$. The obtained lattice constants, internal parameter, the axial ratio c/a, and equilibrium volume for the ReB_2 at $P = 0$ and $T = 0$ are listed in Table 1, together with other theoretical results [7–11] and the experimental data [25]. Our results are in good agreement with the experimental data and other theoretical results.

3.2. The equation of state

To investigate the thermodynamic properties of ReB_2, we carry out total energy electronic structure calculations over a wide range of primitive cell volumes V, i.e., from $0.8V_0$ to $1.2V_0$, where V_0 is the zero pressure equilibrium primitive cell volume. No constraints are imposed on the c/a ratio, i.e., both lattice parameters a and c are optimized simultaneously. At each volume V, it can be found the minimum total energy for the given each u, which obtained the optimized u. Then, we determine the corresponding equilibrium ratio c/a by performing the total energy electronic structure calculations on a series of different values of c/a. For a fixed value of c/a, a series of different values of a are set to calculate the total energies E, which are minimized as a function of the c/a ratio for a given V. Through these calculations, we can obtain the equilibrium lattice parameters a and c as well as the corresponding equilibrium ratio $c/a$for any pressure. The energy–volume (E–V) curve can be obtained by fitting the calculated E–V results to the