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# First-principles calculations of structural and thermodynamic properties of $BeB_2$ compound*

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The lattice parameter, bulk modulus and pressure derivative of $BeB_2$ are calculated by using the Cambridge Serial Total Energy Package (CASTEP) program in the frame of density function theory. The calculated results agree well with the average experimental data and other theoretical results. Through the quasi-harmonic Debye model, the dependences of the normalized lattice parameters $a/a_0, c/c_0$ and the normalized primitive cell volume $V/V_0$ on pressure $P$, the variation of the thermal expansion coefficient $\alpha$ with pressure $P$ and temperature $T$, as well as the dependences of the heat capacity $C_V$ on pressure $P$ and temperature $T$ are obtained systematically.

**Keywords:** local density approximation, thermodynamic properties, $BeB_2$
**PACC:** 7115M, 6740K, 7470E

## 1. Introduction

Since the recent discovery of superconductivity in the relatively simple binary $MgB_2$ at its critical high temperature $T_c$ (39 K),[1] studies of intermetallics containing boron have been particularly interesting and fruitful. As isostructural diborides, $BeB_2$ is isoelectronic with $MgB_2$ and $M_{Mg}/M_{Be} = 2.25$. In the frame of BCS theory (named for its creators, Bardeen, Cooper and Schrieffer), the lighter elements may be conducive to the occurrence of higher frequency phonons and hence increase transition temperature. One expects to obtain even higher $T_c$ by substituting Be for Mg in $MgB_2$ due to the lighter Be atom. Unfortunately, though $BeB_2$ has the same structure as $MgB_2$ belonging to $AlB_2$-type structure with space grope $P6/mmm$, it has been recently reported that there exists no indication of superconductivity down to 5 K in $BeB_2$[2] or only at about 1 K for the complex $BeB_{2.75}$ structure.[3] Medverdeva *et al*[4] have found that the fermi-surface topology of $BeB_2$ is sufficiently modified from that of $MgB_2$ and concluded that there is no medium-$T_c$ superconductivity in $BeB_2$ with the $AlB_2$-type structure. These negative findings make it interesting and necessary to investigate the structure and physical properties of $BeB_2$ in detail.

To our knowledge, there have been made only a few investigations of $BeB_2$. In 1995, Tupisyn *et al*[5] reported the average experimental lattice constants for $BeB_2$, i.e. $a = 2.94$ Å and $c = 2.87$ Å. Applying a full-potential linearized augmented plane wave (FP-LAPW) method, Satta *et al*[6] and Ravindra *et al*[7] studied the ground state electronic structure and some properties of $BeB_2$. Also applying the FP-LAPW method, Profeta *et al*[8] studied the electronic and superconducting properties of $MgB_2$ and $BeB_2$. Recently, Islam *et al*[9] studied the elastic and electronic properties of $BeB_2$ by ab initio CRYSTAL98 program. However, up to now, there have existed no theoretical lattice parameters and thermodynamic properties available for $BeB_2$.

In this work, we investigate the structural and thermodynamic properties of $BeB_2$ compound under high pressures and high temperatures through the Cambridge Serial Total Energy Package (CASTEP) program[10,11] and the GIBBS code based the quasi-harmonic Debye model,[12] in which the phononic effect is considered. The results obtained are in agreement with the available experimental data and those obtained by using other theoretical methods. In Section 2, we briefly review the theoretical method. The results and discussion are presented in Section 3.

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# 2. Theoretical method

## 2.1. Total energy electronic structure calculations

In our electronic structure calculations, we apply the ultrasoft pseudopotentials introduced by Vanderbilt[13] to the interactions of the electrons with the ion cores, together with the Local Density Approximation proposed by Vosko *et al*[14] to exchange-correlation potential. The electronic wave functions are expanded in a plane wave basis set with an energy cut-off of 550 eV. Pseudo-atom calculations are performed for Be $2s^2$ and B $2s^2 2p^1$. For the Brillouin-zone sampling, we use the $12 \times 12 \times 12$ Monkhorst–Pack mesh,[15] where the self-consistent convergence of the total energy is $10^{-6}$eV/Atom. All the electronic structure calculations are implemented through the CASTEP code.[10,11]

## 2.2. Thermodynamic properties

To investigate the thermodynamic properties of $BeB_2$, we apply the quasi-harmonic Debye model,[12] in which the phononic effect is considered. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ can be written in the form of

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

where $E(V)$ is the total energy per unit cell for $BeB_2$, $PV$ corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and $A_{\rm Vib}$ is the vibrational Helmholtz free energy, which can be written as[16,17]

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

Here $D(\Theta/T)$ represents the Debye integral, and $n$ is the number of atoms per formula unit. For an isotropic solid, $\Theta$ is expressed as[16]

$$\Theta_{\rm D} = \frac{\hbar}{k}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}}, \quad (3)$$

where $M$ is the molecular mass per unit cell; $B_{\rm S}$ is the adiabatic bulk modulus, which is approximated given by the static compressibility[16,17]

$$B_{\rm S} \cong B(V) = V\left\{\frac{{\rm d}^2 E(V)}{{\rm d}V^2}\right\}; \quad (4)$$

$f(\sigma)$ is given by Refs.[18,19]; the Poisson $\sigma$ is taken as 0.25.[20] Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume $V$

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \quad (5)$$

By solving Eq.(5), one can obtain the thermal equation-of-equation (EOS) $V(P,T)$. The heat capacity $C_V$ and the thermal expansion coefficient $\alpha$ are given by[19]

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

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (7)$$

where $\gamma$ is the Grüneisen parameter, which is defined as

$$\gamma = -\frac{{\rm d}\ln\Theta(V)}{{\rm d}\ln V}. \quad (8)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of $BeB_2$ at any pressure and temperature from the calculated $E$-$V$ data at $T = 0$ and $P = 0$. By using the method above, we can successfully obtain the thermodynamic properties of GaAs,[21] BN[22] and $Li_2O$.[23]

# 3. Results and discussion

Firstly, we make first-principles calculations to find the most stable structure of $BeB_2$. Since the average experimental axial ratio $c/a$ of $BeB_2$ is 0.976,[5] we thus calculate a series of $c/a$ ratios between 0.951 and 1.04. For a given ratio $c/a$, a series of different lattice parameters $a$ and $c$ are set so as to calculate the total energies $E$ and the corresponding primitive cell volume $V$. In Fig.1, we illustrate some of the $E$-$V$ curves for several values of ratio $c/a$. It is found that a ratio $c/a$ of 0.987 has the minimum energy, which corresponds to the most stable structure of $BeB_2$ at $P = 0$ and $T = 0$. By fitting the calculated energy–volume ($E$–$V$) data to the Natural strain EOS,[24] we have

$$P = 2B_0 \left(\frac{V_0}{V}\right) f_N \left[1 + \frac{3}{2}\left(B' - 2\right) f_N + \frac{3}{2}\left(1 + B^0 B'' + \left(B' - 2\right) + \left(B' - 2\right)^2\right) f_N^2\right], \quad (9)$$

where $f_N = \ln\left(l/l_0\right)$, which may be written as $f_N = \ln\left(V/V_0\right)/3$ for hydrostatic compression. And then we can obtain the lattice parameters $a$, $c$, bulk modulus $B_0$ and pressure derivative $B_0'$ of $BeB_2$, which are listed in Table 1, together with the average experimental data[5] and other theoretical results.[6−9] The agreement between them is good.

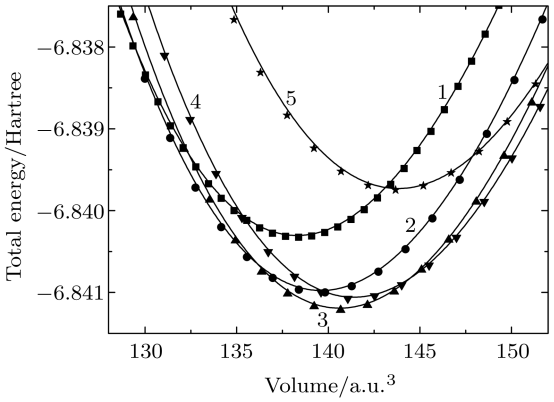



**Fig.1.** The energy–volume curves for different values of ratio $c/a$: 0.951, 0.971, 0.987, 1.0, and 1.04, which are corresponding to curves 1, 2, 3, 4, and 5 respectively.

**Table 1.** The calculated lattice parameters, bulk moduli $B_0$ and pressure derivatives $B_0'$, together with the average experimental data and other theoretical results.

| | $a$/Å | $c$/Å | $c/a$ | $B_0$/GPa | $B_0'$ |
|---|---|---|---|---|---|
| Present work | 2.900 | 2.861 | 0.987 | 210.23 | 3.4 |
| Ref. [6] | 2.903 | 2.853 | 0.983 | | |
| Ref. [7] | 2.886 | 3.088 | 1.027 | 193 | 3.47 |
| Ref. [8] | 2.905 | 2.853 | 0.982 | | |
| Ref. [9] | 2.916 | 2.852 | 0.998 | 215 | 2.7 |
| Exp.[5] | 2.94 | 2.87 | 0.976 | | |

Now, applying the quasi-harmonic Debye mode described above, we investigate the pressure dependence of the lattice parameters, with the pressure varying from −20 to 60 GPa. The normalized lattice parameters $a/a_0$, $c/c_0$ and the ratio $c/a$ (where $a_0$ and $c_0$ are the zero pressure equilibrium lattice constants) as well as the normalized primitive cell volume $V/V_0$ as functions of pressure are illustrated in Fig.2. By fitting these data to third-order polynomials in pressure, we obtain the following relationships at $T = 0$ K:

$$a/a_0 = 1.0000 - 0.00117P + 8.14256 \times 10^{-6}P^2 - 1.69816 \times 10^{-8}P^3, \quad (10)$$

$$c/c_0 = 1.0000 - 0.00279P + 3.18763 \times 10^{-5}P^2 - 2.7583 \times 10^{-7}P^3, \quad (11)$$

$$c/a = 1.0000 - 0.0016P + 2.17569 \times 10^{-5}P^2 - 2.44108 \times 10^{-7}P^3, \quad (12)$$

$$V/V_0 = 1.0000 - 0.00518P + 5.58885 \times 10^{-5}P^2 - 3.75387 \times 10^{-7}P^3. \quad (13)$$

It is seen that, as the pressure increases, the equilibrium ratio $c/a$ of $BeB_2$ ranges from 0.993 at zero pressure to 0.968 at 20 GPa, i.e. decreases by about 2.52% (2.60% for $MgB_2$[25]). The interlayer linear compressibility, $\mathrm{d}\ln c/\mathrm{d}P = 0.00383\,\mathrm{GPa}^{-1}$ is about 1.71 times the basal plane value, $\mathrm{d}\ln a/\mathrm{d}P = 0.00224\,\mathrm{GPa}^{-1}$ (for $MgB_2$, $\mathrm{d}\ln c/\mathrm{d}P = 0.00353\,\mathrm{GPa}^{-1}$, $\mathrm{d}\ln a/\mathrm{d}P = 0.00196\,\mathrm{GPa}^{-1}$[25]). These results show that the compression along the $c$-axis is considerably larger than along the $a$-axis in the basal plane and hence implies that the compression of interlayer B–Be bonds is weaker than that of the intralayer B–B bonds.

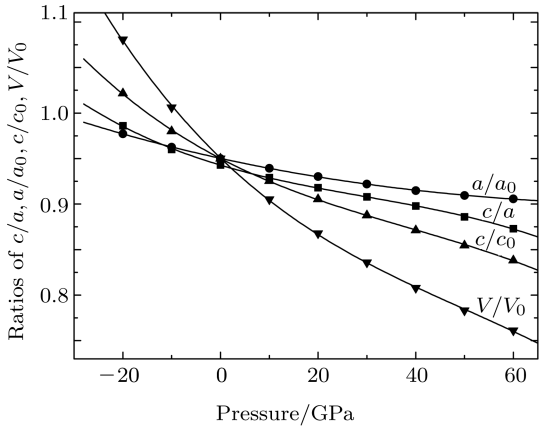



**Fig.2.** The normalized parameters $a/a_0$, $c/c_0$, $c/a$ and $V/V_0$ as functions of pressure at 0 K.

Moreover, we also investigate the temperature dependence of lattice parameters with temperature increasing from 0 to 1000 K. At zero pressure, the equilibrium lattice parameters $a/a_0$, $c/c_0$, the ratio $c/a$ and the normalized volume $V/V_0$ as functions of temperature are plotted in Fig.3. By fitting these data to third-order polynomials in $T$, we obtain the following relationships at $P = 0$ GPa:

$$a/a_0 = 1.0000 - 2.07082 \times 10^{-6}T + 1.57256 \times 10^{-8}T^2 - 6.39072 \times 10^{-12}T^3, \quad (14)$$

$$c/c_0 = 1.0000 - 3.53945 \times 10^{-6}T + 2.82329 \times 10^{-8}T^2 - 8.70353 \times 10^{-12}T^3, \quad (15)$$

$$c/a = 1.0000 - 1.45956 \times 10^{-6}T + 1.24359 \times 10^{-8}T^2 - 2.38928 \times 10^{-12}T^3, \quad (16)$$

$$V/V_0 = 1.0000 - 7.68984 \times 10^{-6}T + 5.96075 \times 10^{-8}T^2 - 2.11109 \times 10^{-11}T^3. \quad (17)$$

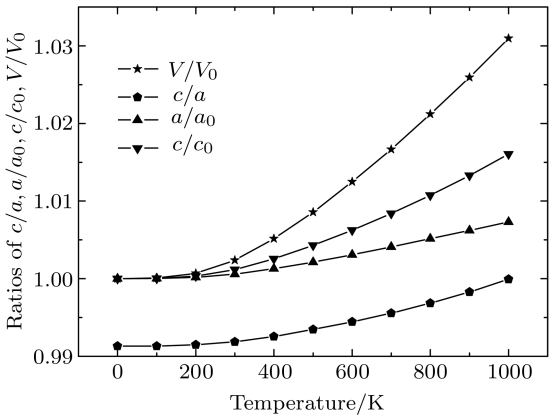



**Fig.3.** The normalized parameters $a/a_0$, $c/c_0$, $c/a$, and volume $V/V_0$ as functions of temperature at 0 GPa.

It is obvious from Figs.2 and 3 that, the lattice constant $c$ is more sensitive to temperature and pressure than the lattice constant $a$, which is consistent with the case of weaker interlayer B–Be bonds. To further investigate the thermal anisotropy, we calculate the linear thermal expansion parameters $\alpha_a$ and $\alpha_c$ in the intralayer and interlayer directions, respectively. Through the following equation at zero pressure:

$$\alpha = \frac{(\Delta l/\Delta T}{l_0} = \frac{1}{l_0}\frac{\partial l}{\partial T}\mid_P \quad (18)$$

where $l$ represents the lattice constants $a$ and $c$, we obtain $\alpha_a = 5.64 \times 10^{-6}\,\mathrm{K}^{-1}$ and $\alpha_c = 1.11 \times 10^{-5}\,\mathrm{K}^{-1}$ at room temperature. In Table 2, we list our results and those of closely related intermetallic compound LiBC[26] and $MgB_2$[27] for comparison. It is found that the thermal expansion along the $c$-axis is 1.97 times that along the $a$-axis, and the interlayer bonding is sort of stronger in $BeB_2$, which indicates that the interlayer covalent interaction of Be-B is a little stronger than that of Mg–B in $MgB_2$ and especially stronger than those of Li–B and Li–C in LiBC.

**Table 2.** The calculated linear thermal expansion parameters at room temperature.

| Compound | | $\alpha_a/10^{-6}\mathrm{K}^{-1}$ | $\alpha_c/10^{-5}\mathrm{K}^{-1}$ |
|---|---|---|---|
| $BeB_2$ | Present work | 5.64 | 1.11 |
| LiBC | Fogg *et al*[26] | 5.59 | 2.83 |
| $MgB_2$ | Jorgensen *et al*[27] | 5.40 | 1.14 |

The Debye temperature is an important fundamental parameter and closely related to many physical properties of solids, such as specific heat and melting temperature. It is known that, at temperatures below the Debye temperature, quantum mechanical effects are very important in understanding the thermodynamic properties, while at temperatures above the Debye temperature quantum effects can be neglected. Thermal expansion parameters, together with the specific heat, are essential for predicting the thermodynamic properties so it is important both practically and theoretically. Therefore, we consider the thermal expansion parameters at temperatures above the Debye temperature and at zero pressure.

From the quasi-harmonic Debye model, we obtain the Debye temperature $\Theta_\mathrm{D} = 1207.66$ K at $P = 0$ and $T = 0$ K, correspondingly, $\alpha_a = -2.07 \times 10^{-6}\,\mathrm{K}^{-1}$ and $\alpha_c = -3.54 \times 10^{-6}\,\mathrm{K}^{-1}$. It is suggested that, the thermal expansion parameters increase along $a$-axis and $c$-axis with increasing temperature, while the in-

crease along $c$-axis is larger than along $a$-axis, which shows that the anisotropy in $BeB_2$ becomes a little stronger with increasing temperature. In Fig.4, we illustrate the thermal expansion coefficient $\alpha$ of $BeB_2$. It is shown that, for a given pressure, $\alpha$ increases with temperature at low temperatures especially at zero pressure and gradually tends to a linear increase at higher temperatures. As pressure increases, the increase of $\alpha$ with temperature becomes smaller. While for a given temperature, $\alpha$ decreases strongly with increasing pressure, and it is very small at higher temperatures and higher pressures.

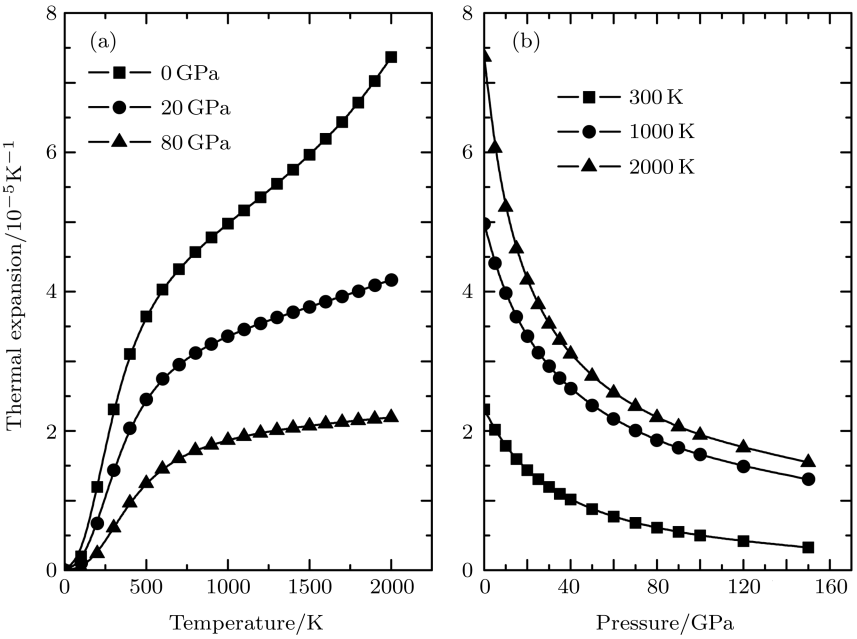



**Fig.4.** The thermal expansion versus pressure and temperature (a) and (b) for $BeB_2$.

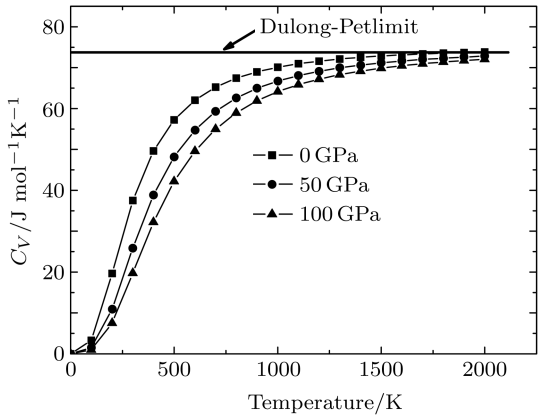



**Fig.5.** The heat capacity of $BeB_2$ versus temperature at different pressures.

The heat capacity of $BeB_2$ at different pressures and temperatures is plotted in Fig.4. It is shown that when $T < 1500$ K, the heat capacity $C_V$ is dependent on temperature and pressure, which is due to the anharmonic approximation of the Debye model used here. However, at higher temperatures, the anharmonic effect on $C_V$ is suppressed, and close to the Dulong–Pettit limit $9Nk(\approx 74.85$ J mol$^{-1}$ K$^{-1})$, which is followed to all solids at high temperatures, where $N$ is Avogadro's constant.

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