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Phase transition and thermodynamic properties of beryllium from first-principles calculations

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ABSTRACT

We have investigated the phase transition, electronic properties, phonon dispersion curves and thermodynamic properties of beryllium (Be) at high pressures and high temperatures using the first-principles calculations based on the density functional theory (DFT). The transition pressure of Be from hexagonal-closed-packed (hcp) structure to body-centered-cubic (bcc) structure occurs at 388 GPa. The calculated phonon dispersion curves agree with experimental results. Under compression, the phonon dispersion curves of hcp Be do not show any anomaly or instability. At low pressure the phonon dispersion curves of bcc Be display imaginary frequencies along Γ–N symmetry line. Within the quasi-harmonic Debye model, the thermal equation of state and other properties including the thermal expansion coefficient, isothermal bulk modulus and its first pressure derivative, heat capacity and entropy of hcp and bcc Be are predicted.

1. Introduction

Due to large compressibility, complex phase diagrams, and simple atomic configuration, the alkaline-earth metals such as beryllium, magnesium, calcium, strontium, and barium are of considerable interest [1]. Beryllium as a light alkaline metal, has anomalous physical properties such as high Debye temperature and extraordinarily low Poisson's ratio [2]. Beryllium has attracted substantial attention because of its technological importance in the field of aircrafts, spacecrafts, communication satellites, and nuclear power industry [3].

The phase transition of Be has been the subject of many experimental and theoretical studies. Crystalline Be is in the hexagonal-closed-packed (hcp) structure with space group $P6_3/mmc$ at ambient conditions [4]. With increasing temperature up to 1523 K [5], Be transforms from hcp structure to body-centered-cubic (bcc) structure. Through experimental measurement technique, any kind of phase transition up to 180 GPa did not detect [6–8]. Many theoretical investigations [9–11] predicted the hcp–bcc phase transition pressure between 100 and 200 GPa. With the full-potential linear muffin-tin orbit (FPLMTO) method, the hcp–bcc phase transition has been predicted to be 270 GPa by Sin'ko and Smirnov [12]. Recently, Benedict et al. [13] and Robert and Sollier [14] predicted the phase boundaries of the hcp–bcc phase transition, and they all found the hcp to bcc phase transition occurs at 400 GPa at 0 K. Up to now, Be is still controversial in phase transition. Therefore, we predict the phase transition using the first-principles method.

The other task for this paper is to theoretically present electronic and dynamical properties of Be under extreme condition. Häussermann and Simak [15] found that the electronic properties of Be is quite different from that of other alkaline-earth metals. The electronic properties of Be crystals at ambient pressure were theoretically studied [16–19]. The low-temperature phonon dispersion curves of hcp Be were measured in neutron scattering experiments [20]. Theoretically, Robert et al. [21] obtained the phonon dispersion curves of hcp Be and bcc Be at different densities using the frozen phonon method. However, relatively less attention has been paid to the electronic and phonon properties of Be under high pressure. Therefore, in this work we concentrate on the electronic and phonon properties of Be under high pressure and temperature.

In this work, we have investigated the phase transition, electronic properties, phonon dispersion curves and thermodynamic properties of Be under high pressures and high temperatures. This paper is organized as follows. In Section 2, we give a detailed description of the theoretical computational methods. The results and detailed discussions are presented in Section 3. Section 4 is a summary of the results and a general conclusion.

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Table 1
The equilibrium volume V_0 (Å^3/atom), lattice parameters a and c, axial ratio c/a, zero pressure bulk modulus B_0 (GPa), and pressure derivative B'.

	V_0	a	c	c/a	B_0	B'
hcp						
Present	7.904	2.263	3.566	1.576	121	3.37
Expt.	8.105 [29]	2.285 [29]	3.585 [29]	1.569 [29]	118 [30]	3.52 [30]
Expt.	8.11 [31]	2.286 [31]	3.584 [31]	1.568 [31]	119 [32]	3.48 [32]
Cal.	7.914 [12]	2.265 [12]	3.563 [12]	1.573 [12]	122 [12]	3.31 [12]
Cal.	7.751 [13]	2.251 [13]	3.534 [13]	1.57 [13]	111.5 [13]	3.69 [13]
bcc						
Present	7.812	2.5			123	3.31

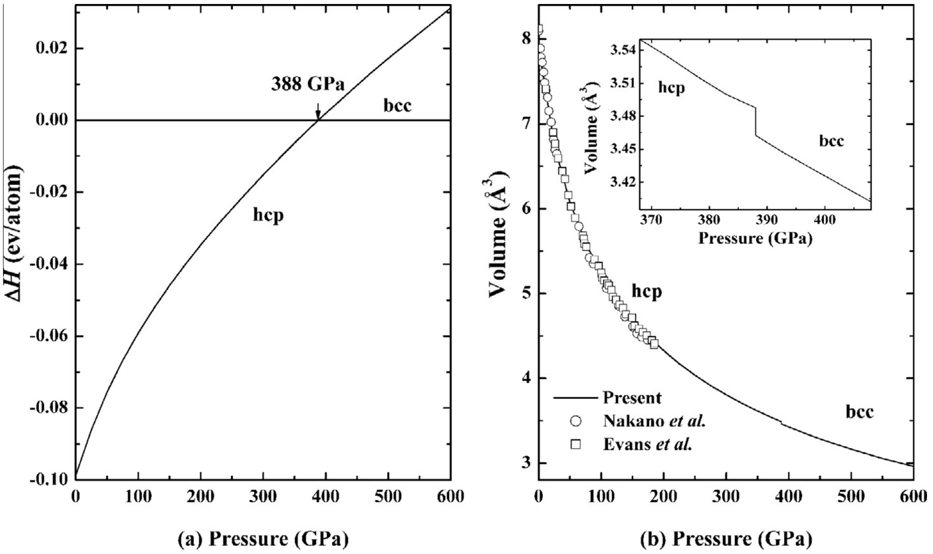

Fig. 1. (a) Enthalpy per atom of hcp Be relative to the enthalpy of bcc Be as a function of pressure. (b) The static equation of state of hcp and bcc Be compared with experimental measurements [6,8].

2. Theoretical methods

The present calculations were performed within the density functional theory (DFT) formalism as implemented within Vienna *ab initio* simulation package (VASP) [22]. For the exchange–correlation functional, the generalized gradient approximation (GGA) of Perdew and Wang (PW91) [23] was employed. The electron-ion interaction was described by ultrasoft pseudopotentials (USPP) [24]. The plane-wave energy cutoff was 600 eV and the self-consistence convergence of the energy was set to 10^{-7} eV/atom. Integrations in the Brillouin zone were performed using special k-points generated with $20 \times 20 \times 14$ and $20 \times 20 \times 20$ mesh for hcp and bcc Be, respectively. The phonon properties were performed using the small displacement method [25]. To ensure the convergence of phonon frequencies, we made careful tests on k-points and other technical parameters. The forces were obtained using first-principles calculations with 128 and 64 atoms for hcp and bcc Be, respectively. To obtain the force constants for the phonon calculations, atomic displacements of 0.03 Å were employed.

To study the temperature and pressure dependence of the thermal properties, the quasi-harmonic Debye model [26,27] allowing for the thermal effects is applied. The non-equilibrium Gibbs function $G^*(V;\, P,\, T)$ is taken in the form of

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

where E (V) is the total energy for per unit cell of Be, PV is the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and A_{vib} is the vibrational Helmholtz free energy, which can be expressed as

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

where n is the number of atoms per formula unit and $D(\Theta/T)$ is the Debye integral. Θ is expressed as

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

where M is the molecular mass per unit cell, σ is the Poisson ratio and B_s is the adiabatic modulus. $f(\sigma)$ is the scaling function, given by Ref. [27]. 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

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

Then, we can obtain the thermal equation of state (EOS) from Eq. (4).

3. Results and discussion

3.1. Phase transition and electronic properties

The static equilibrium lattice parameters, bulk modulus and its pressure derivative of hcp and bcc Be are obtained by fitting the energy–volume (E–V) data to the fourth-order finite strain EOS [28]:

$$P = 3B_0 f_E(1 + 2f_E)^{5/2}\left\{1 + \frac{3}{2}(B' - 4)f_E + \frac{3}{2}\left[B_0B'' + (B' - 4)(B' - 3) + \frac{35}{9}\right]f_E^2\right\}, \tag{5}$$