



Thermodynamic properties of MgO under high pressure from first-principles calculations

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Abstract

The equations of state (EOS) and other thermodynamic properties of the rocksalt (RS) structure MgO are investigated by *ab initio* plane-wave pseudopotential density functional theory method. The obtained results are consistent with the experimental data and those calculated by others. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of relative volume V/V_0 on pressure P , cell volume V on temperature T , and Debye temperature Θ and specific heat C_V on pressure P are successfully obtained. The variation of the thermal expansion α with temperature and pressure is investigated, which shows the temperature has hardly any effect on the thermal expansion α at higher pressure.

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1. Introduction

Accurate equations of state and other thermodynamic properties for crystalline materials are very important in many applications involving

high pressure and high temperature. As one of the major earth-forming minerals, periclase (MgO) is stable in rocksalt (RS) structure with the pressure up to 227 GPa. This unique structural stability makes MgO an ideal standard for calibrating pressure in experiments at extreme conditions. Therefore, the equations of state and the other thermodynamic properties of MgO at elevated pressures and temperature are of great interest to physicist and geophysicist in experimental investigations [1–7] and theoretical studies [8–12].

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In experiment, Duffy et al. [1] reduced the isothermal volume compression relation at 300 K. Jackson and Niesler [2] measured the isothermal bulk modulus and its pressure derivative of MgO by ultrasonic interferometric technique with the pressure up to 3 GPa. Using the shock compression data of MgO at the pressure up to 199 GPa together with the Mie–Grüneisen equation, Sino-geikin and Bass [3] investigated the equations of state (EOS) and the elastic modulus of MgO. Moreover, Fiquet et al. [4] measured the thermal expansivity α at one atmospheric pressure ($1 \text{ atm} = 1.013 \times 10^{-4} \text{ GPa}$). Fei [5] carried out the diamond-anvil-cell static compression experiments of MgO up to 23 GPa at 300 K. Using the radial X-ray diffraction and the Brillouin spectroscopy measurement, Zha et al. [6] investigated the elasticity and pressure–density EOS of MgO up to 55 GPa, and Merkel et al. [7] studied the elastic moduli, shear strength, and elastic anisotropy up to 47 GPa.

In theory, Allan et al. [8] calculated the 300 K isotherm using two-body potentials and a simple shell model. Wolf and Bukowinski [9] investigated the 300 K isothermal with the electron–gas model. The static and thermal EOS were obtained from the static and ab initio molecular dynamics simulations performed using the projector augmented-wave and pseudopotential method [10]. Matsui et al. [11] simulated the structural and the thermodynamic properties of crystals by combining the molecular dynamics (MD) method with quantum corrections to the MD values over a wide range of temperatures and pressures. Karki et al. [12] investigated the thermal expansivity of MgO using the density functional perturbation theory [13] within the local density approximation [14]. They derived the heat capacity and the entropy from the calculated spectra.

In this work, we focus on investigating the EOS and the other thermodynamic properties of the RS structure MgO in the range of 0–170 GPa by the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) program [15,16] and by the quasi-harmonic Debye model [17], which allows us to obtain all thermodynamics

quantities from the calculated energy–volume points. We have successfully obtained the lattice constant, the bulk modulus B_0 , the pressure derivative of bulk modulus and the elastic constants for the RS structure MgO.

2. Theoretical methods

In the electronic structure calculations, we use the norm-conserving pseudopotential in Kleinman–Bylander representation generated using the optimization scheme of Lin et al. [18] in order to reduce the required value of the plane-wave energy cut-off. The generalized gradient approximation (GGA) exchange–correlation function [19] is represented by Perdew–Wang (PW) formula. A plane-wave basis set with energy cut-off 295.00 eV is applied. Pseudo atomic calculations are performed for Mg $3s^2$ and O $2s^2 2p^4$. For the Brillouin-zone sampling, we use the $10 \times 10 \times 10$ Monkhorst-Pack mesh, where the self-consistent convergence of the total energy is at 10^{-6} eV/atom . All the total energy electronic structure calculations are implemented through the CASTEP code [15,16].

To investigate the thermodynamic properties of MgO, we here apply the quasi-harmonic Debye model [17], in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of [17]

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

where $\Theta(V)$ is the Debye temperature, and the vibrational term A_{vib} can be written as [20,21]

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

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed by [20]

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

where M is the molecular mass per formula unit, B_S the adiabatic bulk modulus, which can be

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