Computational Materials Science 154 (2018) 159–168

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Fundamental properties and phase stability of B1 and B2 phases of MgO over a wide range of pressures and temperatures: A first-principles study

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ARTICLE INFO

Keywords:
Lattice dynamics
Thermal properties
Equation of state
Phase transformations
High-pressure

ABSTRACT

Accurate determination of the phase diagram of MgO is proved to be a challenging task, mainly because of the very high B1–B2 transition pressures (P_t) and melting temperatures. Only very recently experimental observations of the B1–B2 and solid-liquid transitions of MgO have been achieved. In spite of the extensive experimental and theoretical studies, a satisfactory agreement about the phase diagram of MgO has not yet been reached. In this work, we will thoroughly investigate the various factors that may affect the calculated B1–B2 phase boundary, using first-principle techniques. The structural, vibrational and thermal properties of the B1 and B2 phases of MgO are also investigated. It has been found that P_t is quite sensitive to the set of pseudopotentials (PPs) used in the PP plane-wave approach, and volume (or pressure, P) range over which the Helmholtz free energy is directly calculated. An interplay between such a P range and the anharmonic effects is demonstrated, which allows (by a suitable choice of the P range) for a high reduction in these effects (i.e., highly extends the validity of the temperature range of the quasiharmonic approximation). The very recently proposed optimized norm-conserving Vanderbilt (ONCV) PPs are found to yield results in very good agreement with those obtained by the all-electron projected augmented wave calculations, contrary to other norm-conserving PPs. As for the exchange-correlation energy, the local density approximation is not only found to provide a good description of P_t of the above transition, but also its temperature dependence. The obtained results are discussed in comparison with the most recent theoretical results and experimental data. In particular, our results suggest that the estimated temperature of the B1–B2 transition directly observed by using the laser-driven ramp loading technique is highly exaggerated.

1. Introduction

Magnesium oxide (MgO, periclase) has recently received a renewed interest because of its geophysical and technological importance, as well as the recent advances in high-pressure experimental techniques by using high-power lasers. At ambient conditions, MgO crystallizes in the rocksalt (B1) structure, before it transforms to the cesium-chloride (B2) phase at extremely high pressure (P), about 600 GPa at low temperatures [1]. Therefore, MgO is currently used as an actual pressure standard at high pressures and high temperatures (T) [2]. It is an end-member ferropericlase, (Mg,Fe) O, thought to be the major non-silicate oxide of the Earth's lower mantle, as well as super-earths (extra-solar planets with masses up to 10 times that of Earth). Moreover, it has numerous applications in a wide range of areas such as medicine, ceramics, catalysis, spintronics, electronics, and microelectronics. Only very recently the experimental observations of the B1–B2 and solid-liquid phase transformations of MgO have been achieved [1,3–6]. These experiments have stimulated several first-principle investigations [4,5,7,8]. Despite these extensive experimental and theoretical research activities, a satisfactory agreement about its P-T phase diagram has not yet been achieved. The main aim of this work is to provide a thorough theoretical investigation of the B1–B2 phase boundary of MgO.

The first experimental evidences of the B1–B2 and B2-liquid transitions of MgO, along the shock Hugoniot line, are provided by the decaying shock measurements of McWilliams et al. [3]. The two anomalies on smoothly decaying shocked MgO at about (450 GPa and 9000 K) and (650 GPa and 14,000 K) are attributed to the above two transitions, respectively. In the more recent decaying shock measurements [6], the anomaly observed at (470 GPa and 9860 K) is associated to the B2-liquid transition. The B1–B2 transition has also been

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https://doi.org/10.1016/j.commatsci.2018.07.035
Received 15 May 2018; Received in revised form 16 July 2018; Accepted 18 July 2018

investigated by using steady shock experiments by Miyanishi et al. [4] and Root et al. [5], and it has been found that the B1 phase is stable up to about 320 and 360 GPa, respectively. These experimental works [4,5] disagree also about B2-liquid transition pressure. On the other hand, Coppari et al. [1] have used a laser-driven ramp loading method to compress MgO up to 900 GPa, and provided the first direct evidence for the B1–B2 transition, at about 600 GPa and an estimated temperature of about 4000 K.

The B1–B2 phase boundary in the *P-T* space of MgO has been the subject of many theoretical investigations [4,5,7–11]. using several approaches ranging from model potential calculations [9] to first-principle methods that take into account the anharmonic effects [5,7,8]. The anharmonic effects are due to the T dependence of the phonon frequencies, arising from the phonon-phonon interactions [i.e., beyond the quasi-harmonic approximation (QHA)]. The most recent first-principle calculations [4,5,7,8,11] have led to a B1–B2 transition pressure (P_t) of about 500 GPa at $T = 0$, but these calculations significantly disagree about its T dependence. At elevated temperatures, the Clapeyron slope (dP_t/dT) obtained in Refs. [7,8], based on a phonon density of states (PDOS) obtained by Fourier transformation of the autocorrelation functions computed by *ab initio* molecular dynamics (AIMD), differ significantly from each other and both are appreciably smaller than that obtained by using other methods [4,5,11]. On the other hand, the temperature above which the anharmonic effects become important is a controversial issue: Root et al. [5] have found that these effects become important above 5000 K, while in Ref. [11] a temperature of about 8000 K is suggested. The finding of Ref. [5] is consistent with the estimation of Wu et al. [12].

The other fundamental properties of MgO have also received considerable interest. Several investigations have been performed to determine more accurately the *P*-volume (*V*)-*T* equation of state (EOS), over extended P and T ranges (see, e.g., Ref. [2]). The lattice thermal conductivity of MgO has been very recently computed from a complete solution of the linearized Boltzmann transport equation, over wide P and T ranges [13]. The thermal properties have been studied [14,15] within QHA and by including the anharmonic effects via simple models. The electrical conductivity and reflectivity along the Hugoniot have been experimentally [3,6] and theoretically [8] investigated, in order to characterize the electronic structure changes under compression. It has been shown that while the B1 and B2 phase remain large band gap semiconductors in the pressure ranges of interest, the liquid phase shows a metallic behavior.

In this work, we performed a thorough first-principles study of the thermal properties of the B1 and B2 structures and B1–B2 phase boundary of MgO, over wide P and T ranges. These properties are computed by using QHA based on accurate phonon frequencies, obtained by employing the density functional perturbation theory (DFPT) and optimized norm-conserving Vanderbilt pseudopotentials (ONCV-PPs) [16]. To investigate the effects of the utilized set of PPs on the B1–B2 phase boundary, similar calculations are performed by employing PPs generated by using the APE code [17] (APE-PPs), and by projected augmented wave (PAW) method [18]. The effects of the adopted exchange-correlation (XC) energy functional on the B1–B2 phase boundary are also investigated, by using the local density (LDA) and generalized gradient (GGA) approximations. Moreover, the effects of the V (or P) range, over which the Helmholtz free-energy is directly computed, on both thermal properties and B1–B2 phase boundary are carefully investigated. In particular, we show how the chosen P range can be used to monitor and highly reduce the anharmonic effects, which allows for accurate calculations of the above properties within the QHA over wide P and T ranges. This finding will allow us also to touch upon the anharmonic effects on the B1–B2 phase boundary of MgO.

The rest of the paper is organized as follows. In Section 2, we briefly describe the methodology used to calculate the free-energies and thermal properties, and the computational details. In Section 3, we report and discuss our results for the structural, vibrational and thermal properties of the B1 and B2 phases, and B1–B2 phase boundary of MgO. Finally, a summary of our main results and conclusions is given in Section 4.

2. Methodology

2.1. Background

The basic quantity from which all the thermal properties are derived is the Helmholtz free energy ($F(V, T)$), which, within the adiabatic or Born-Oppenheimer approximation, can be written as

$$F(V, T) = E_0 + F_{vib} = E_0 + E_{vib} - TS_{vib}. \tag{1}$$

Here, E_0 is the calculated total energy, and E_{vib} and S_{vib} are the contributions of the lattice vibration to the internal energy and entropy (S), respectively. The electronic contribution to S vanishes identically for large band gap semiconductors, like MgO, and hence it is not included in Eq. (1). F_{vib} is usually computed by using the QHA (i.e., it is calculated in the harmonic approximation, retaining only the V dependence of the phonon frequency), and within this approximation Eq. (1) becomes

$$F(V, T) = E_0(V) + k_B T \sum_{\mathbf{q}} \sum_{j} \ln\left\{2\sinh\frac{\hbar\omega_{j,\mathbf{q}}(V)}{2k_B T}\right\}, \tag{2}$$

where $\omega_{j,\mathbf{q}}$ is the frequency of the j^{th} phonon mode at wavevector $\mathbf{q}$.

The structural properties and EOS (P versus V) at a given T are determined by computing $F(V, T)$ at several volumes, and fitting the calculated values to third order Birch-Murnaghan [19] EOS. The transition pressure of the B1–B2 phase transformation at a given T is obtained from the condition of equal Gibbs free energy,

$$G(V, T) = F(V, T) + P(V, T)V, \tag{3}$$

where the pressure, at a given T and V, is

$$P(V, T) = -\left(\frac{\partial F(V, T)}{\partial V}\right)_T. \tag{4}$$

Due to anharmonicity effects, the heat capacity at constant P (C_P) is different from that at constant V (C_V). The former, which is what experiments directly determine, is proportional to T at high T, while the latter goes to a constant that is given by the classical equipartition law, $C_V = 3Nk_B$, where N is the number of atoms in the system. The relation between C_P and C_V, at a certain point in the *P-T* space, is [20]

$$C_P - C_V = \alpha_V(P, T)^2 B(P, T) V(P, T) T, \tag{5}$$

where B is the bulk modulus, and α_V is the thermal expansivity. C_V is given as

$$C_V(T) = \sum_{\mathbf{q}} \sum_{j} c^V_{j,\mathbf{q}} = k_B \sum_{\mathbf{q}} \sum_{j} \left(\frac{\hbar\omega_{j,\mathbf{q}}(V)}{2k_B T}\right)^2 \frac{1}{\sinh^2\left[\hbar\omega_{j,\mathbf{q}}(V)/2k_B T\right]}. \tag{6}$$

Here, $c^V_{j,\mathbf{q}}$ is the contribution to C_V of the $(j, \mathbf{q})$ phonon mode at a given T, and V corresponds to the given P.

In this work, $\alpha_V(P, T)$, as a function of T at a given P, is calculated by employing the Grüneisen formula [21]

$$\alpha_V(P, T) = \frac{1}{BV} \sum_{\mathbf{q}} \sum_{j} \gamma_{j,\mathbf{q}} c^V_{j,\mathbf{q}}, \tag{7}$$

where $\gamma_{j,\mathbf{q}} = -\frac{d\ln\omega_{j,\mathbf{q}}}{d\ln V}$ is the mode Grüneisen parameter. Here, B, V and $c^V_{j,\mathbf{q}}$ correspond to the given point in the $P-T$ space, and $\gamma_{j,\mathbf{q}}$ is assumed to be T independent and calculated at the zero temperature V corresponding to the given P.