Ab initio study of MgO under pressure using quasi-harmonic approximation

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Abstract. We examine the dependence of the Gibbs free energy and entropy on pressure and density along MgO isotherm 300 K. Some theoretical works have previously predicted a drastic drop of entropy along MgO isotherms by analyzing existing experimental data and extrapolating them to high pressures. We present first-principle calculations of thermodynamic properties of MgO under pressure using density functional theory and quasi-harmonic approximation. The robustness of our calculations is verified by comparing the calculated and experimental phonon dispersion curves. The comparison with available diamond anvil cell experimental data is also provided. Our estimate for the B1–B2 phase transition is in good agreement with other experimental and theoretical studies. However, our results for entropy along isotherm 300 K do not agree with previous theoretical estimates based upon the integration of thermal expansion coefficient and isothermal bulk modulus by volume.

1. Introduction
Magnesium oxide (MgO) is an important component of the mantle of the Earth and extrasolar planets [1]. It is commonly used as a representative mantle material in exoplanet modeling [2]. That is why there are a lot of studies dedicated to the determination of MgO properties under extreme conditions, in particular at high pressures. Dynamic compression experiments with MgO to pressures of TPa range [3, 4] revealed a structural transformation. Magnesium oxide is expected to change from a rocksalt (B1) to a caesium chloride (B2) crystal structure at pressures 400–600 GPa [3–11]. Recent first-principle calculations at $T = 0$ K narrow this range to 475–510 GPa [9–11].

Entropy can be considered as one of the most important thermodynamic properties. While a temperature dependence of entropy can be determined by measuring the temperature dependent heat capacity at constant pressure by differential scanning calorimetry [12], a compression dependence of entropy cannot be found directly from experiment. There are theoretical works [13,14] on entropy calculation by integrating the product of thermal expansion coefficient and isothermal bulk modulus, which predict a drastic drop of entropy along isotherms and even a tendency towards negative values in the vicinity of the phase transition at 300 K [15]. Some researchers interpret such behavior as an entropy crisis in the system and assume that near-zero entropy values are precursors or drivers of the MgO structure transformation [16,17].
On the other hand, entropy can be effectively calculated using first-principle calculations based on density-functional theory (DFT) [18]. Finite temperature effects at $T = 300$ K can be taken into account using quasi-harmonic approximation (QHA) [19]. Thus, DFT+QHA can be an efficient tool to determine whether a drastic drop of entropy occurs and there is an entropy crisis in the system in the vicinity of the MgO polymorphic phase transition. In this work we calculate entropy along the isotherm 300 K using DFT+QHA for both B1 and B2 phases of MgO. Besides, we examine the parameters of the B1–B2 phase transition and compare our results with previous works. We also present a comparison of the DFT+QHA phonon dispersion curves for MgO at 300 K with experimental data [20, 21] to demonstrate our calculations correctness. The results of our work might be useful for the construction of wide-range semiempirical equations of state with taking into account the polymorphic transformations in particular [22, 23].

2. Methods and parameters

2.1. First-principle and quasi-harmonic approximation

Helmholtz free energy in the QHA can be represented as a sum of three terms:

$$ F(V, T) = E_c(V) + F_{ph}(V, T) + F_{el}(V, T), $$

where the cold energy of a crystal $E_c(V)$ and electronic term $F_{el}(V, T)$ can be found using first-principle calculations based on DFT. To calculate the contribution of the phonon subsystem the following expression is used:

$$ F_{ph}(V, T) = k_B T \sum_{\mathbf{q}, j} \ln \left( 2 \sinh \left( \frac{\hbar \omega_{\mathbf{q}, j}(V)}{2k_B T} \right) \right), $$

where $\omega_{\mathbf{q}, j}$ is a frequency of mode $j$ at some $\mathbf{q}$ point, $k_B$ is the Boltzmann constant.

Knowing the Helmholtz free energy, the Gibbs free energy can be found using the following thermodynamic relationship:

$$ G(V, T) = F(V, T) - V \frac{\partial F(V, T)}{\partial V} T. $$

Therefore the entropy of the phonon subsystem in the QHA can be represented as

$$ S_{ph}(V, T) = -k_B \sum_{\mathbf{q}, j} \left[ \ln \left( 2 \sinh \left( \frac{\hbar \omega_{\mathbf{q}, j}(V)}{2k_B T} \right) \right) - \frac{\hbar \omega_{\mathbf{q}, j}(V)}{2k_B T} \coth \left( \frac{\hbar \omega_{\mathbf{q}, j}(V)}{2k_B T} \right) \right]. $$

Meanwhile, the following expression for entropy is used in works [13, 14]:

$$ S(T, \eta) = V_0 \int_1^\eta \alpha K_T d\eta + S(T, 1), $$

where $\alpha$ is the thermal expansion coefficient, $K_T$ is the isothermal bulk modulus, $\eta = V/V_0$ is the relative volume.

2.2. Details of first-principle calculations

We used Vienna Ab initio Simulation (VASP) [24, 25] package to perform DFT calculations and Phonopy [26] code for evaluation of phonon frequencies using the finite displacement method. All DFT calculations were performed within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [27, 28] for the exchange-correlation functional. The electron–ion interaction is described with the projector augmented wave (PAW) method [29], where 10 and 6 electrons are considered as valence for Mg and O, respectively. The applicability of the chosen pseudopotentials was accurately checked at high pressures by making a comparison with more accurate pseudopotentials [30].
Figure 1. Phonon dispersion curves for MgO at $T = 300$ K under normal pressure: lines—our calculations; dots—experimental data [31].

A plane-wave cutoff energy $E_{\text{cut}}$ was 500 eV. Calculations for the B1-structure were performed for a $2 \times 2 \times 2$ supercell containing 64 atoms and a $3 \times 3 \times 3$ supercell with 54 atoms was used for the B2-structure of MgO. We applied a $11 \times 11 \times 11$ $k$-point mesh with the Monkhorst–Pack generation scheme for the sampling of the Brillouin zone of the B1 phase and $15 \times 15 \times 15$ $k$-point mesh for the B2 phase. A $60 \times 60 \times 60$ $q$-point grid was used for the phonon modes sampling.

3. Results

Before performing calculations for the two phases of MgO under pressure, we checked how well our pseudopotentials reproduce the properties of MgO in the B1 phase at normal conditions. Comparison of computed phonon dispersion curves for the B1 phase with experimental data [31] is presented in figure 1. The non-analytical term correction to the dynamical matrix was applied to treat long range interaction of macroscopic electric field induced by polarization of collective ionic motions near the $\Gamma$-point, which is responsible for a splitting of the frequencies of the optical vibrational modes parallel and perpendicular to the electric field (the so-called LO-TO splitting) [32, 33].

We also compared the calculated isotherms for the B1 and B2 phases at 300 K with data from experiments on static compression in diamond anvil cells [20, 21]. The results are presented in figure 2. Both figures show very good agreement between our results and experiments. Results of dynamic compression by laser-driven ramp loading [4] are also shown in figure 2 to demonstrate an experimental evidence of the phase transition. Structural measurements performed during the experiment indicated a structural transformation from B1 to B2 crystal structure at pressures of about 400–600 GPa. It is worth noting that temperature was rising during the ramp loading so the direct comparison between our results and this experiment is meaningless.
Figure 2. Isotherm 300 K for MgO in the pressure–relative density plane: solid blue and green lines—B1 and B2 structures respectively from this study; black and white symbols—data of diamond anvil cell experiments (circles—[20]; triangles—[21]); blue and green circles—results from laser-based dynamic compression experiment [4]; blue circles represent B1-structure of MgO, while green ones represent B2-structure observed in the experiment. The supposed area of the phase transition is marked with green and taken from [4].

The Helmholtz free energy for the B1 and B2 phases was found from equation (1). Since we know the cell volume and pressure in the crystal, we can find Gibbs free energy using equation (3). The Gibbs energy for the B1 phase was taken as reference energy. The dependence of the Gibbs energy difference for the two phases is presented in figure 3. We determined the value of pressure of the phase transition as 510.4 GPa. Our estimate for the pressure of the B1–B2 phase transition is in good agreement with another theoretical study [34] and experimental data [4].

Entropy was found from equation (4). Concurrently, our results are in good agreement with previous works [35], where it was shown that QHA is applicable up to 1000 K for MgO. The results for the B1 and B2 phases are presented in figure 4. Our calculations predict a small positive entropy jump of \( \Delta S = 0.07 \text{ kJ/mol} \) at the phase transition. Accompanied by a negative jump in volume, it leads to a negligible negative Clausius–Clapeyron slope \( \frac{dP}{dT} \) at 300 K. This result is consistent with previous theoretical estimates [10, 11, 34, 36].

Further comparison of our results with theoretical works [13, 14] in which equation (5) was used for entropy estimations is shown in figure 5. It is clearly seen, that our curve for entropy of the B1 phase along isotherm 300 K is higher than those predicted in [13, 14]. Our first-principle QHA calculations do not demonstrate a dramatic drop of entropy while approaching the vicinity of the phase transition.
**Figure 3.** Difference between Gibbs energies of B2 and B1 phases of MgO versus pressure in the vicinity of polymorphic transition B1–B2.

**Figure 4.** Dependence of entropy upon pressure for MgO at \( T = 300 \) K: the region of B1–B2 phase transition is shown enlarged in the inset.
4. Conclusion
Using DFT and QHA we calculated free energy, phonon properties and B1–B2 phase transition of MgO. Our results are consistent with previous experimental and theoretical works. Our estimate for the pressure of B1–B2 phase transition of MgO is 510.4 GPa, that agrees with other experimental and theoretical studies. DFT+QHA results for entropy differ from previous theoretical calculations, based on the integration of the product of thermal expansion and isothermal bulk modulus. Our calculations do not predict a sharp drop of entropy while approaching the phase transition region. Further research of the behavior of the thermal expansion coefficient and the isothermal bulk modulus along isotherms is required to determine the cause of the discrepancy.

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