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# First-principles calculations on MgO: Phonon theory versus mean-field potential approach

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Various thermodynamic properties of MgO were studied using both *ab initio* phonon theory and the mean-field potential (MFP) approach. They include thermal pressure, thermal expansion, the 300 K equation of state, and the shock Hugoniot. It is found that the results of *ab initio* phonon theory and the MFP approach agree with each other, except that *ab initio* phonon theory gave a poor description of the thermal pressure when temperature became relatively high. © 2006 American Institute of Physics. [DOI: 10.1063/1.2219081]

## I. INTRODUCTION

MgO is one of the most important constituents of the Earth's lower mantle. Knowledge of its thermal properties at high temperatures and pressures is required for a better understanding of many geophysical phenomena. MgO has also been considered as a potential internal pressure standard since no pressure-induced phase transition is observed at pressures up to 200 GPa. An enormous amount of theoretical and experimental effort has been devoted to obtain its thermodynamic parameters.

Experimentally, the thermodynamic property of condensed matter at megabar pressures can now be probed in both static, low-temperature diamond-anvil cell (DAC) experiments,<sup>1–6</sup> and in dynamic, high-temperature shock-wave experiments.<sup>7–10</sup> The DAC technique is suitable for ordinary laboratory in which samples can be studied under controlled conditions. Using laser heating and refinements in instrumentation, temperatures of about 3000 K can be reached up to pressures of the order of 200–300 GPa, while at room temperature Ruoff *et al.*<sup>11</sup> reported an ultrahigh DAC pressure of 560 GPa. Even higher temperature and pressure conditions can be achieved by shock-wave methods. Accordingly, there is a need to develop a theoretical method that can be used to facilitate the interpretation of the new data at extreme conditions of temperature and pressure.<sup>12,13</sup>

On the theoretical side, to calculate the structural and thermodynamic properties at finite temperatures, the contribution of lattice thermal vibration to the total free energy needs to be taken into account. The commonly accepted method is lattice dynamics, or phonon approach. In this theory, the harmonic and quasiharmonic approximations are typically employed.<sup>14,15</sup> The expansion of lattice potential in a series of powers of atomic displacement is truncated at the

second-order term; hence, the normal-mode transformation allows for the Hamiltonian of the system to be expressed as a sum of non-interacting one-dimensional harmonic Hamiltonians. The physical concept of “phonon” is then introduced naturally since the energy eigenvalue spectrum for a parabolic potential consists of equally spaced energy levels that makes an energy excitation look like a simple increase in the number of particles. There have been many lattice dynamics calculations,<sup>16–19</sup> and very good agreement has been achieved between the calculated and observed phonon dispersion curves at low temperatures. However, the phonon approach to a real system may become less accurate at high temperatures where the harmonic approximation may no longer be valid.

Other previous theoretical efforts on MgO include, but are not limited to, the studies of its equation of state,<sup>20–24</sup> elasticity,<sup>17,25–27</sup> the B1-B2 structural phase transition,<sup>25,28,29</sup> and melting curve, both classically<sup>28–30</sup> and *ab initio* quantum mechanically.<sup>31,32</sup>

Taking the experimental data on thermal expansion, adiabatic bulk modulus, and specific heat at constant pressure as input, and using fundamental thermodynamic relations [such as those below Eq. (1)], Anderson and Zou<sup>12</sup> calculated the complete set of thermodynamic functions of MgO for the temperature range 300–2000 K and the pressure range 0–150 GPa. Since this work contains the most extensive compilation of the thermodynamic functions of MgO that can be found in the literature, we will use it as a comparison to the present work.

In our prior studies,<sup>33–37</sup> we developed a classical MFP approach to calculate the various thermodynamic quantities of a (typical) metal. The MFP approach has been tested on a number of metal systems, including Na, Be, Ce, U, Th, Al, Cu, Ta, Mo, and W at different pressures and temperatures. In this work, we extend this approach to the more compli-

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cated nonmetallic system of MgO. A calculation using the traditional phonon theory was also performed for comparison.

The rest of this paper is organized as follows. In Sec. II we present the basic formula of the MFP approach in parallel with the traditional phonon theory. The details of the calculations are given in Sec. III. In Sec. IV we present our calculated thermodynamic properties. Finally, Sec. V contains our summary.

## II. MFP APPROACH AND PHONON THEORY

MgO is an isolator with a large energy band gap. Thermal electronic excitations are hence negligible. Therefore, at a given averaged atomic volume  $V$  and temperature  $T$ , the Helmholtz free energy per ion  $F(V, T)$  can be written as the sum of the cold ( $T=0$ ) energy ( $E_c$ ) and the ionic vibration energy ( $F_{\text{ion}}$ )

$$F(V, T) = E_c(V) + F_{\text{ion}}(V, T). \quad (1)$$

For a metal, Eq. (1) would contain another term,  $F_{\text{el}}(V, T)$ , the electronic excitation free energy.

Other thermodynamic functions can be obtained from  $F(V, T)$  through fundamental thermodynamic relations; for example, entropy is  $S = -(\partial F / \partial T)_V$ , internal energy is  $E = F + TS$ , pressure is  $P = -(\partial F / \partial V)_T$ , and the Gibbs free energy is  $G = F + PV$ . The specific procedures of computing  $F_{\text{ion}}$  using both the MFP approach and the traditional phonon theory are discussed below.

### A. MFP approach

We first give a brief summary of the MFP approach.<sup>33</sup> It is known that the vibrational contribution to the partition function takes the form  $Z_{\text{ion}} = \exp(-NF_{\text{ion}}/k_B T)$ , where  $N$  is the total number of lattice ions. In the mean-field approximation, the classical  $Z_{\text{ion}}$  is given by<sup>33</sup>

$$Z_{\text{ion}} = \left( \frac{M k_B T}{2 \pi \hbar^2} \right)^{3N/2} \left\{ \int \exp[-g(\mathbf{r}, V)/k_B T] d\mathbf{r} \right\}^N. \quad (2)$$

Therefore,

$$F_{\text{ion}}(V, T) = -k_B T \left( \frac{3}{2} \ln \frac{M k_B T}{2 \pi \hbar^2} + \ln \nu_f(V, T) \right), \quad (3)$$

where

$$\nu_f(V, T) = 4 \pi \int \exp\left(-\frac{g(r, V)}{k_B T}\right) r^2 dr. \quad (4)$$

The essential feature of the MFP approach is that the mean-field potential  $g(\mathbf{r}, V)$  is simply constructed in terms of the 0 K total energy  $E_c$  alone, which is obtained from *ab initio* electronic structure calculations

$$g(r, V) = \frac{1}{2} [E_c(R+r) + E_c(R-r) - 2E_c(R)]. \quad (5)$$

It was shown<sup>33</sup> that the well-known Dugdale-MacDonald<sup>38</sup> expression for the Grüneisen parameter can be derived by expanding  $g(r, V)$  in a series of powers of  $r$  to order  $r^2$ .

It should be noted that the MFP approach is only suitable at relatively high temperatures, since the classical approximation is employed.

### B. Phonon theory

Under the quasiharmonic approximation, the vibration free energy of the lattice ions  $F_{\text{ion}}$  is given by<sup>39</sup>

$$F_{\text{ion}}(V, T) = k_B T \sum_{\mathbf{q}} \sum_j \ln \left\{ 2 \sinh \left[ \frac{\hbar \omega_j(\mathbf{q}, V)}{2 k_B T} \right] \right\}, \quad (6)$$

where  $\omega_j(\mathbf{q}, V)$  represents the frequency of the  $j$ -th phonon mode at wave vector  $\mathbf{q}$ .

In a sense, the phonon theory is more rigorous than the MFP approach since no further approximation is adopted except for the harmonic one. However, it is well known that the phonon theory may become invalid at high temperatures where the vibrations of the lattice ions become anharmonic.<sup>40,41</sup>

## III. CALCULATION DETAILS

In all of our electronic structure calculations for MgO, we employed the local density approximation (LDA) as implemented by Ceperley and Alder.<sup>42</sup> The 0 K total energy  $E_c$  in Eq. (1) was obtained using the full-potential linearized augmented plane wave (LAPW) method.<sup>43,44</sup> To calculate the phonon frequency  $\omega_j(\mathbf{q}, V)$  in Eq. (6), we used the plane-wave self-consistent field (PWSCF) method<sup>45</sup> based on the *ab initio* linear-response theory. The 0 K calculations were done at different lattice parameters in an increment of 0.1 a.u.

At a given temperature  $T$ ,  $F(V, T)$  in Eq. (1) was calculated at the same lattice parameter as for the 0 K calculation. Then the cubic spline interpolation was employed to find the minimum of  $G(P, T) = F(V, T) + PV$  as a function of  $V$ . That is, we did not use the Grüneisen approximation to derive the other thermodynamic quantities from Eq. (6).

## IV. RESULTS AND DISCUSSIONS

### A. Phonon dispersion

This subsection is only relevant to the phonon theory. Experimentally, the phonon frequency can be measured directly by inelastic neutron scattering.<sup>46</sup> To validate the *ab initio* phonon calculations, perhaps the most important and interesting step is to calculate the phonon dispersion. In Fig. 1, our results are compared to the inelastic neutron scattering measurements along the high symmetry lines in the Brillouin zone (BZ).<sup>47</sup> There are already many phonon calculations on MgO published by others.<sup>16–19</sup> Our results are consistent with the other calculations as well as with the experiment.

### B. Thermal pressure

The first quantity that we want to use to compare the MFP approach and the phonon theory is the temperature dependence of the “thermal pressure”  $(\partial P / \partial T)_V$ , which is equal to  $\beta_P * B_T$ , the product of the thermal expansion coefficient and the isothermal bulk modulus.<sup>48</sup> Geophysical models typi-

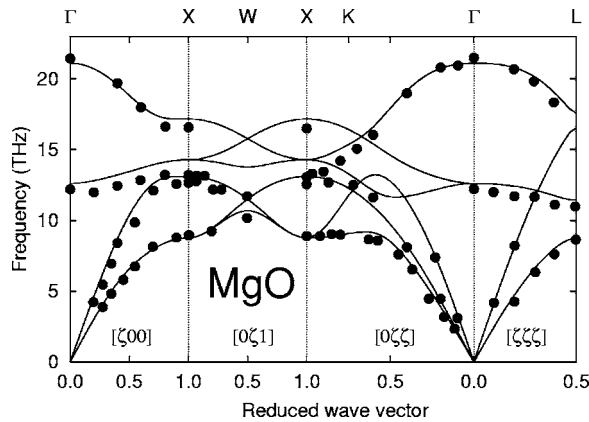


FIG. 1. Phonon dispersion of MgO. Solid line: present calculation; solid circles: measurements by Sangster *et al.*<sup>47</sup>

cally assume that for mantle minerals  $\beta_P \cdot B_T$  is independent of both volume and temperature. The calculated variation with a temperature of  $\beta_P \cdot B_T$  at ambient pressure is illustrated in Fig. 2 both for the MFP approach and the phonon theory. Also shown in this figure are the zero-pressure values of  $\beta_P \cdot B_T$  by Anderson and Zou,<sup>12</sup> and those by Dubrovinsky and Saxena<sup>49</sup> directly from experiment.

The experimentally determined  $\beta_P \cdot B_T$  (Refs. 12 and 49) increases with  $T$  between 300 and 1000 K, and then decreases for  $T > 1000$  K. The phonon theory indeed reproduced well the temperature dependence of  $\beta_P \cdot B_T$  for  $T < 500$  K. However, for  $T > 1000$  K, the phonon theory still predicted a steady increase of  $\beta_P \cdot B_T$ , which is in contradiction with experiment.<sup>12,49</sup> Interestingly, the MFP approach reproduced well the temperature dependence of  $\beta_P \cdot B_T$  for  $T > 1000$  K.

### C. Thermal expansion

Shown in Fig. 3 are the calculated volume thermal expansion coefficients  $\beta_P$  for MgO using both the MFP approach and the phonon theory, along with the values given by Anderson and Zou<sup>12</sup> ( $\beta_P$  is the prefactor in the product  $\beta_P \cdot B_T$ ). It is seen that our results on  $\beta_P$  obtained using the phonon theory do not converge for  $T > 2000$  K, whereas those by Karki *et al.*<sup>17</sup> show convergence up to 3000 K. The

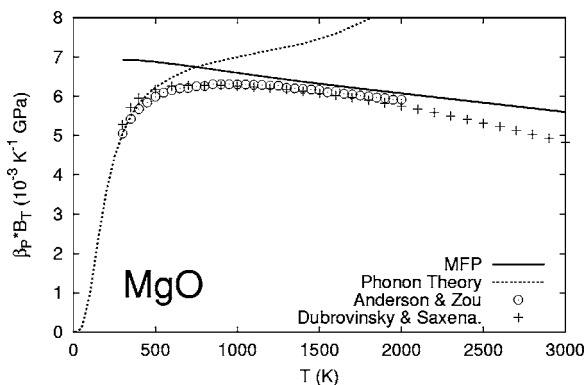


FIG. 2. Temperature dependence of thermal pressure  $\beta_P \cdot B_T$  for MgO at ambient pressure. Solid line: MFP; dashed line: phonon theory; open circles: empirical thermodynamic calculation by Anderson and Zou;<sup>12</sup> pluses: measurements by Dubrovinsky and Saxena.<sup>49</sup>

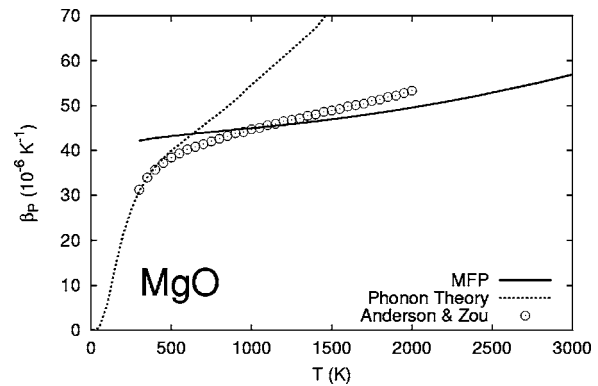


FIG. 3. Thermal expansion coefficient for MgO at ambient pressure. Solid line: MFP; dashed line: phonon theory; open circles: empirical thermodynamic calculation by Anderson and Zou.<sup>12</sup>

plausible explanation for the difference is that Karki *et al.* used the 0 K Grüneisen parameter obtained in Ref. 17 in which higher-order anharmonic effects were neglected. We emphasize once again that we calculated  $F_{\text{ion}}(V, T)$  using Eq. (6) at several volumes near the equilibrium value, to find the minimum of  $F(V, T)$  in Eq. (1) by the spline interpolation, and thus we did not adopt the Grüneisen approximation.

### D. 300-K equation of state

Our calculated 300 K equation of state (EOS) is shown in Fig. 4, in the form of  $V/V_0$  versus  $P$ . For MgO, especially while compressed, 300 K means “low” temperature, as also seen from its thermal expansion shown in Fig. 3. Strictly speaking, the predicted thermal expansion by the MFP approach is not accurate at low temperatures. Fortunately, the thermal effects on the 300 K EOS are very weak. Indeed, the calculated 300 K EOS by the MFP approach and the phonon theory are indistinguishable (within the plot resolution) in Fig. 4. Another observation is that LDA for MgO produced excellent agreement with both experiment<sup>1–6</sup> and empirical modeling.<sup>12,13</sup>

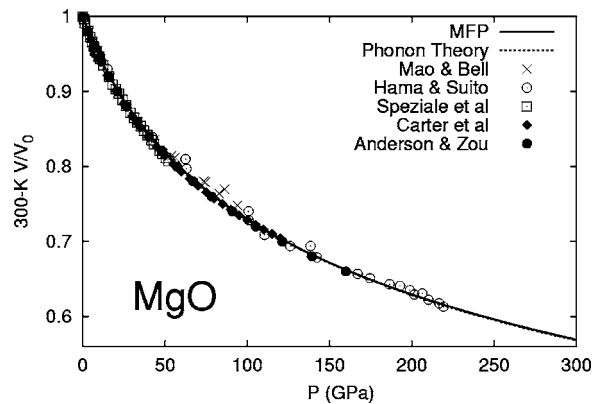


FIG. 4. 300 K EOS for MgO. Solid line: MFP; dashed line: phonon theory; crosses: DAC experiment by Mao and Bell;<sup>2</sup> open circles: corrected measurements by Duffy *et al.*<sup>3</sup> and Hama and Suito;<sup>4</sup> open squares: DAC experiment by Speziale *et al.*<sup>5</sup> solid diamonds: reduced shock data by Carter *et al.*<sup>13</sup> solid circles: empirical thermodynamic calculation by Anderson and Zou.<sup>12</sup>



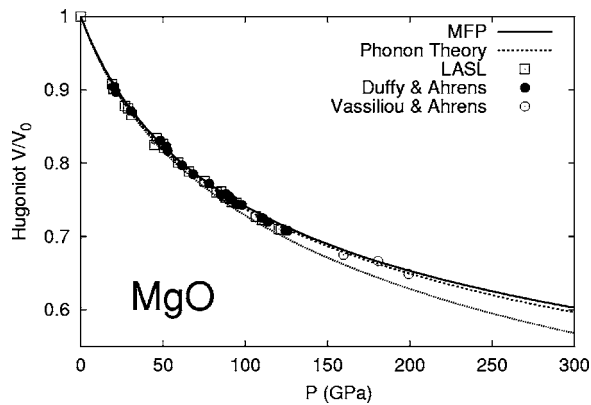


FIG. 5. Principal Hugoniot of MgO. Solid line: MFP; dashed line: phonon theory; open squares: LASL shock Hugoniot data;<sup>7</sup> solid circles: measurements by Duffy and Ahrens;<sup>8</sup> open circles: measurements by Vassiliou and Ahrens.<sup>9</sup> Dotted line is the calculated 300 K EOS plotted to illustrate the relative thermal pressure between the Hugoniot EOS and the 300 K EOS.

### E. Shock Hugoniot

The Hugoniot state,<sup>7</sup> produced by shock-wave compression, is the most suitable subject for being studied with the MFP approach. The temperature increase, which comes from the deposited impact energy, makes the classical approximation especially suitable.

The  $P$ - $V$  Hugoniot was obtained from the Rankine-Hugoniot relation  $P(V_0 - V)/2 = E - E_0$ , where  $V_0$  is initial specific volume and  $E_0$  is the initial specific internal energy. Figure 5 shows that again, as for the 300 K EOS, the Hugoniot EOS obtained using the MFP approach and the phonon theory are very close to each other, and agreement with experiments<sup>7-9</sup> is again excellent.

### F. Temperature along the principal Hugoniot

The last comparison between the MFP approach and the phonon theory is made for the calculation of the temperature along the principal Hugoniot for MgO. The results are shown in Fig. 6 along with the measured temperatures by Svendsen and Ahrens.<sup>10</sup> We see no difference between the MFP approach and the phonon theory in the pressure range of 0–300 GPa.

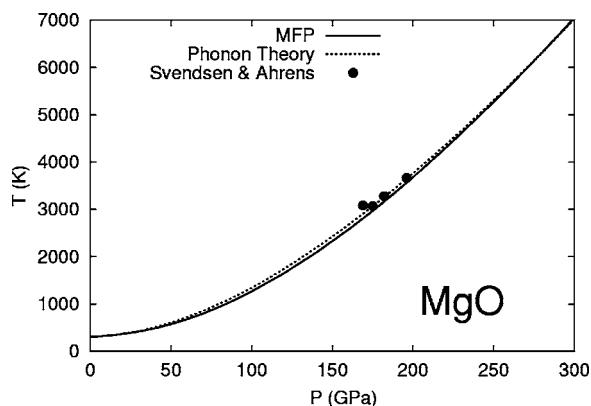


FIG. 6. Temperature along the principal Hugoniot of MgO. Solid line: MFP; dashed line: phonon theory; solid circles: reduced temperature data by Svendsen and Ahrens.<sup>10</sup>

## V. SUMMARY

The various thermodynamic properties of MgO were calculated using the phonon theory and the mean-field potential (MFP) approach. Under the quasiharmonic approximation, the phonon density of states is calculated as a function of lattice parameter and then the thermal contribution to the Helmholtz free energy is derived. Within the classical approximation, the MFP approach is more efficient because only the total energy at 0 K as a function of the lattice parameter is needed. The agreement between the two methods for the compressed state is excellent, while the MFP approach can predict thermal pressure  $\beta_P^* B_T$  better than the phonon theory when the temperature becomes relatively high at ambient pressure. Experiments show that when temperature reaches about 1000 K,  $\beta_P^* B_T$  would decrease with increasing temperature. Such a decrease was theoretically predicted using the MFP approach.

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