Vibrational and thermodynamic properties of forsterite at mantle conditions

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[1] We present a first-principle study of the vibrational and thermodynamic properties of Mg2SiO4 forsterite up to 20 GPa. The calculated local density approximation (LDA) frequencies and their pressure dependence are in good agreement with the available Raman and infrared spectroscopy data. We also predict the pressure dependence of the modes which are yet to be measured. Thermodynamic properties are obtained using the quasi-harmonic approximation (QHA) to the free energy in conjunction with these results. The calculated pressure-volume-temperature (P-V-T) relations and thermodynamic properties agree well with the reported experimental data within the regime of validity of the QHA. The only discrepancies with experimental data that point to intrinsic anharmonic effects are the mode Gruneisen parameters of two Raman and one infrared modes. However, their effect on thermodynamic properties appears to be negligible.


1. Introduction

[2] Mg2SiO4 forsterite is the end-member of olivine, which is the major constituent of the upper mantle. It has been widely studied; the results can be seen in both vibrational spectroscopy [Akaogi et al., 1984; Chopelas, 1990; Ghose et al., 1992; Gillet et al., 1991; Hofmeister, 1987; Ishi, 1978; Pilati et al., 1995; Rao et al., 1988; Wang et al., 1993] and elasticity measurements [Cynn et al., 1998; Downs et al., 1996; Duffy et al., 1995; Guyot et al., 1996; Isak et al., 1989; Li et al., 1996; Meng et al., 1993; Zha et al., 1994]. Vibrational modes of forsterite measured at high pressure in the laboratory are limited in its number of detected modes (84 modes for forsterite in total) even though the stability of forsterite reaches 410 km depth of the Earth. Previous lattice dynamic calculations [Pavese, 1998; Price et al., 1987] on forsterite are limited to the usage of empirical potentials. The first-principles approach based on density functional theory [Hohenberg and Kohn, 1964] has been successfully applied to predict the structural and elastic properties of Mg2SiO4 forsterite at high pressures [da Silva et al., 1997; Wentzcovitch and Stixrude, 1997], while the vibrational properties are yet to be explored with this approach.

[3] In the past decade, first-principles lattice dynamics in conjunction with the quasi-harmonic approximation (QHA) has been applied to predict vibrational and thermodynamic properties of mantle minerals such as MgO pericalse [Karki et al., 2000c], MgSiO3 perovskite [Karki et al., 2000b], MgSiO3 ilmenite [Karki et al., 2000a], MgSiO3 postperovskite [Tsuchiya et al., 2004; Tsuchiya et al., 2005], and Mg2SiO4 ringwoodite [Yu and Wentzcovitch, 2006] at mantle conditions. The predicted vibrational and thermoelastic properties of these minerals and their aggregates have been reported to be in very good agreement with available experimental data and preliminary reference Earth model (PREM). Now we address the properties of Mg2SiO4 forsterite with the same methods. In contrast, with these other minerals, Mg2SiO4 forsterite is stable at low pressures up to 14 GPa. Some studies have reported anharmonic characteristics in forsterite [Anderson, 1996; Cynn et al., 1996; Gillet et al., 1991] based on the observation of the temperature dependence of the Raman and acoustic frequencies, in addition to thermodynamic considerations by which CV was determined from measurements of Cp. Here we will compare the calculated and measured vibrational properties of forsterite and investigate the validity of the QHA formulation to reproduce its thermodynamic properties.

2. Method

[4] Our computations use the local density approximation (LDA) [Ceperley and Alder, 1990; Perdew and Zunger, 1981]. Calculation details are similar to those reported in previous works [Karki et al., 2000b; Tsuchiya et al., 2004; Tsuchiya et al., 2005; Yu and Wentzcovitch, 2006]. The equilibrated structure of forsterite was calculated using the first-principles implementation of a variable cell-shape damped molecular dynamics (VCSMD) [Wentzcovitch and Price, 1996; Wentzcovitch et al., 1995]. Pseudopotentials of Mg were generated by the method of von Barth and Car [Karki et al., 2000b;
Tsuchiya et al., 2005], while those of O and Si are by
the method of Troullier and Martins [Troullier and
Martins, 1991]. The plane wave energy cut-off used is
70 RY, and the k point sampling of the charge density
was performed on a 2 × 2 × 2 grid in Brillouin zone
(BZ) shifted by 1/2, 1/2, 1/2. The calculations with 2 × 2 ×
2 and 4 × 2 × 4 grid of k points give a difference in
energy by 0.1 meV/atom, in pressure by 0.03 GPa. Thus
using 4 × 2 × 4 grid changes little on the precision for
this study. The dynamical matrix was obtained using
density functional perturbation theory (DFPT) [Baroni
et al., 2001]. At each pressure, dynamical matrices were
calculated on a 2 × 2 × 2 (without shift) q point mesh;
force constants were extracted and used to produce matrices in a 12 × 12 × 12 q point grid. The corresponding normal modes were used in the calculation of the free energy.

3. Results and Discussion

Forsterite has an orthorhombic structure (Pbnm,
Z = 4). Mg atoms occupy two distinct octahedral sites:
M1 (4a) and M2 (4c); Si atoms occupy the tetrahedral
site (4c); O atoms occupy three distinct sites at tetrahe-
dral corners: O1 (4c), O2 (4d), and O3 (8d). The oxygen
atoms form a distorted hexagonal close-packed arrange-
ment. The unit cell has four formulas (28 atoms), so
there are 84 vibrational modes at each q point in the
Brillouin zone, among which 3 are acoustic and 81 are
optical modes. The irreducible representation of forsterite lattice at the BZ center is as in equation (4a)

\[ \Gamma_{op} = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 14B_{1u} + 10B_{2u} + 14B_{iu} \]  

(4a)

where 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} are Raman active; 14B_{1u} + 10B_{2u} + 14B_{3u} are infrared active; and 10A_u is inactive. The three acoustic modes are B_{1u} + B_{2u} + B_{3u}.

The calculated phonon dispersion along several sym-
metry directions and the vibrational densities of states at 0
and 20 GPa are shown in Figure 1. The diagonal com-
ponents of the dielectric tensor are (2.85, 2.77, 2.79) at zero
pressure and (2.33, 2.77, 2.79) at 20 GPa. The Born
effective charges of Mg are close to 2 for Mg, while those
for Si and O are significantly different from ideal values of
4 and -2 and are highly anisotropic. For Mg, they are
Z*[Mg] = (2.17, 1.72, 1.94) at 0 GPa and (2.11, 1.71, 1.89)
at 20 GPa; Z*[Si] = (3.07, 2.62, 2.92) at 0 GPa and (3.10,
2.74, 2.99) at 20 GPa; Z*[O1] = (-2.33, -1.40, -1.47) and
Z*[O2] = (-1.60, -1.98, -1.53) at 0 GPa, and Z*[O1] =
(-2.27, -1.42, -1.49) and Z*[O2] = (-1.58, -1.61,
-1.85) at 20 GPa.

We list our calculated frequencies of the optical
Raman modes at 0 GPa and 0 K in Table 1, infrared
modes in Table 2, and inactive modes at zone center in
Table 3 and compare these with previously reported results
at 0 GPa pressure. Also, listed are the mode Gruneisen
parameters \( \gamma_i = -d\ln(\omega)/d\ln V \). A number of studies have
reported the phonon frequencies of forsterite at zero
pressure using different techniques such as Raman and
infrared spectroscopy [e.g., Iishi, 1978; Lam et al., 1990]
and inelastic neutron scattering [Rao et al., 1988]; only the
results from one study [Iishi, 1978] are listed in Tables 1
and 2, since these studies agree well with each other. The
frequency of an infrared active mode splits into two values
depending on whether the mode is longitudinal (LO) or
transverse (TO), which is due to the contribution of the
macroscopic electric field to the LO mode in a polar
crystal. The calculated eigenvectors, which contain informa-
tion about the internal and external motions of the SiO_4
tetrahedral and Mg ions, are used to deduce the symmetry
labels of the modes following a method described else-
where [Rao et al., 1988]. We find similar frequency-
pressure relationships between Raman and infrared modes.
The calculated frequencies at the zone center are all
positive and increase with pressure for Raman (Figure 2a)
infrared modes alike (Figure 2b). The pressure
dependences of mode frequencies are consistent with
available experimentally fitted curves [Chopelas, 1990;
Hofmeister, 1987; Wang et al., 1993]. Only two Raman
modes, the lowest B_{3g} ones and one B_{1u} IR mode, have
the calculated \( \gamma_i \) considerably different from measured
ones. This might be signs of forsterite’s anharmonicity,
not properly accounted for by the present approach.
Table 1. Vibration Raman Modes of Forsterite at Ambient Conditions in cm⁻¹

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experiment</th>
<th>(\nu_1)</th>
<th>(\gamma_i)</th>
<th>Modes Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_8</td>
<td></td>
<td>188</td>
<td>0.30</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td></td>
<td>222</td>
<td>0.75</td>
<td>227</td>
</tr>
<tr>
<td></td>
<td></td>
<td>316</td>
<td>1.21</td>
<td>305</td>
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<td>333</td>
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<td>357</td>
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<td>436</td>
<td>1.36</td>
<td>424</td>
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<td></td>
<td>529</td>
<td>0.77</td>
<td>546</td>
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<td></td>
<td>596</td>
<td>0.69</td>
<td>609</td>
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<td></td>
<td>818</td>
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<td></td>
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<td>850</td>
<td>0.42</td>
<td>856</td>
</tr>
<tr>
<td>B_3</td>
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<td>195</td>
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<td>226</td>
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<td></td>
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<td>1.07</td>
<td>318</td>
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<td>383</td>
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<td></td>
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<td>418</td>
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<td>412</td>
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<td></td>
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<td>577</td>
<td>0.58</td>
<td>595</td>
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<td>914</td>
<td>0.36</td>
<td>922</td>
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<td>B_2</td>
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<td>1.27</td>
<td>441</td>
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<td>568</td>
<td>0.57</td>
<td>588</td>
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<td>222</td>
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<td>327</td>
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<td>384</td>
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<td>569</td>
<td>0.61</td>
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<td></td>
<td>618</td>
<td>0.68</td>
<td>632</td>
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<td>829</td>
<td>0.48</td>
<td>839</td>
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<td>858</td>
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<td>975</td>
<td>0.59</td>
<td>976</td>
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</table>

*The assignments follow a previous study [Iishi, 1978]. R (rotational lattice mode) and T (translational lattice modes) are the two external modes. The four internal vibrational modes of SiO₄ ion are \(v_1\) (A₃ type), \(v_2\) (E type), \(v_3\) (F₂ type). References: a, [Iishi, 1978]; b, [Lam et al., 1990]; c, [Gillet et al., 1991]; d, [Wang et al., 1993]; and e, [Chopelas, 1990]. \(\nu_i\) is the vibrational frequency; \(\gamma_i\) is the Grüneisen parameter of mode \(i\) as defined in equation 5b.

However, their effect on thermodynamics properties seems to be unnoticeable within the regime of validity of the QHA.

4. Thermodynamic Properties

[8] In the QHA formulation, the Helmholtz free energy can be expressed as:

\[
F(V, T) = U_0(V) + \frac{1}{2} \sum_{q,j} \hbar \omega_j(q, V) + k_B T \sum_{q,j} \ln (1 - \exp(-\hbar \omega_j(q, V)/k_B T))
\]

(4b)

where the first term is the internal energy, the second is the zero point motion energy, and the third is the vibrational energy contribution, where \(\omega_j\) represents phonons with normal mode \(q\). The total vibrational energy of a crystal is the sum over all the phonon modes in the Brillouin zone.

In our calculation, the sum is performed on a \(12 \times 12 \times 12\) mesh, i.e., 343 inequivalent points in the first BZ. When comparing predictions of the QHA with measurements, it is important to be aware of the domain of validity of this model.

Table 2. Calculated Frequencies (cm⁻¹) of Infrared Modes of Forsterite, Compared With Experiments at Zero Pressure

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experiment</th>
<th>(v_{\nu=0})</th>
<th>(v_{\nu=0})</th>
<th>(\gamma_i)</th>
</tr>
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<tbody>
<tr>
<td>A_8</td>
<td></td>
<td>205</td>
<td>205</td>
<td>1.16</td>
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<td></td>
<td></td>
<td>277</td>
<td>277</td>
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<td>296</td>
<td>297</td>
<td>1.04</td>
</tr>
<tr>
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<td>323</td>
<td>1.12</td>
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<td></td>
<td>407</td>
<td>450</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
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<td>482</td>
<td>482</td>
<td>1.00</td>
</tr>
<tr>
<td>B_3</td>
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<td></td>
<td></td>
<td>954</td>
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</table>

*The assignments follow a previous study [Iishi, 1978]. R (rotational lattice mode) and T (translational lattice modes) are the two external modes. The four internal vibrational modes of SiO₄ ion are \(v_1\) (A₁ type), \(v_2\) (E type), \(v_3\) (F₂ type). References: a, [Iishi, 1978]; b, [Wang et al., 1993]; c, [Hofmeister, 1987]. \(\nu_i\) is the vibrational frequency; \(\gamma_i\) is the Grüneisen parameter of mode \(i\) as defined in equation 5b.

Table 3. Calculated Frequencies (cm⁻¹) and Mode Grüneisen Parameters for A_4 Inactive Modes at Zero Pressure

<table>
<thead>
<tr>
<th>(\nu_1)</th>
<th>(\nu_4)</th>
<th>(\gamma_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>171</td>
<td>0.98</td>
</tr>
<tr>
<td>180</td>
<td>161</td>
<td>0.16</td>
</tr>
<tr>
<td>246</td>
<td>225</td>
<td>0.69</td>
</tr>
<tr>
<td>299</td>
<td>286</td>
<td>1.17</td>
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<td>348</td>
<td>347</td>
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<td>390</td>
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<td>439</td>
<td>437</td>
<td>1.31</td>
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<tr>
<td>495</td>
<td>495</td>
<td>0.95</td>
</tr>
<tr>
<td>509</td>
<td>511</td>
<td>0.86</td>
</tr>
<tr>
<td>905</td>
<td>885</td>
<td>0.37</td>
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</table>
The maximum temperature at which the QHA is predictive at a particular pressure can be inferred from a posteriori inspection of the thermal expansion coefficient, $\alpha(T)$. There is, in general, a deviation from the linearity of $\alpha(T)$ at high $T$, i.e., at some $T$ between the Debye temperature ($\sim 750^\circ C$) and the melting temperature ($\sim 2160^\circ C$); the zero point of $\partial^2\alpha/\partial T^2$ can be used to bind the QHA validity region (Wentzcovitch et al., 2004). Using this criterion, our results indicate that QHA is valid for forsterite in the upper mantle (Figure 3). In the following, we present our results and compare them with experimental data, from which we can see the effectiveness of the QHA. The results at pressure and temperature regions (P-Ts) where the QHA is valid are plotted as solid line, otherwise plotted as dotted line. Differences between calculations and measurements can also be seen in the QHA invalid P-T region. Although we have not done so, anharmonicity in this P-T domain could perhaps be accounted for by introducing in equation (4b) a term of $a_v K_0 T^2$ where $a_v = (\partial \ln v/\partial T)_v$ defined by Downs et al. [1996], Gillet et al. [1991], and Guyot et al. [1996]. There are limited data $a_v$ available; only 20 out of 81 modes have been reported [Downs et al., 1996; Gillet et al., 1991; Guyot et al., 1996], thus it is difficult to apply this procedure to this study.

The calculated pressure-volume-temperature (P-V-T) relations are plotted in Figure 4. These curves are fitted with isothermal third-order finite strain equations [Birch, 1986] yielding $V_0 = 289.5 \, \text{Å}^3$, $K_0 = 126.4 \, \text{GPa}$, $\tilde{E}_0 = 4.2$. These compression curves are in good agreement with the experimental data [Downs et al., 1996; Gillet et al., 1991; Meng et al., 1993, 106; Guyot et al., 1996]. A comparison of calculated and measured thermodynamic properties at room temperature and pressure is reported in Table 4. The agreement between calculated and measured values is excellent.

In Figures 5a–5g, the calculated thermodynamical properties are plotted and compared with reported data as a function of pressure and temperature. The isothermal

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**Figure 2.** Pressure dependence of the frequencies of (a) Raman vibrational modes, (b) infrared TO, (c) infrared LO, and (d) inactive mode at the zone center. Cross symbols are calculated frequencies. The solid line and dashed line are experimentally extrapolated results.

**Figure 3.** The valid pressure and temperature region of QHA estimated from calculated thermal expansion coefficient. The thick line indicates an estimate of geotherm [Brown and Shankland, 1981; Green et al., 1999], the light gray region is the QHA valid region.
agreement with experimental data within the range of validity of the QHA. At higher pressure, the effect of anharmonicity caused by temperature is expected to decrease. The estimated thermal expansivity at 10 GPa by Guyot et al. [1996] is in excellent agreement with our predictions even beyond the QHA permitted region. Below 1000 K, the differences at 10 GPa are probably due to usage of a less than suitable functional form for \( \alpha(T) \) to fit experimental data.

In the QHA, Gr"uneisen parameters \( \gamma_{th} \) and \( \gamma_m \) derived from equations (5a) and (5b), are equal.

\[
\gamma_{th} = \frac{\alpha K_f V}{C_V} \tag{5a}
\]
\[
\gamma_m = \frac{\Sigma(\gamma_i C_i)(/C_i)}{\Sigma C_i}
\]
\[
\gamma_i = -\left( \partial \ln(\omega_i) / \partial \ln V \right)\_T
\]
\[
C_V = k(h\nu/kT)^2 \exp(h\nu/kT) / [\exp(h\nu/kT) - 1]^2
\]

where \( C_V \) is the heat capacity at constant volume. \( \omega_i \) is the phonon frequency of a vibrational mode \( i \); \( C_{Vi} \) is the Einstein heat capacity, and \( \gamma_i \) is the mode Gr"uneisen parameter of mode \( i \); \( \gamma_m \) is defined as Gr"uneisen parameter in terms of the vibrational modes. The comparison between \( \gamma_{th} \) and \( \gamma_m \) for major earth minerals are explicitly discussed in two other studies [Anderson, 1989; Chopelas, 2000]. The discrepancies between \( \gamma_{th} \) and \( \gamma_m \) exist in most minerals such as forsterite, ringwoodite, modified spinel, and MgO. Previously reported Raman spectroscopic measurements [Gillet et al., 1991] have demonstrated that the value of \( \gamma_m \) derived from equation (5b) is too small compared to reported \( \gamma_{th} \) derived from equation (5a) [Chopelas, 1990], which may be due to intrinsic anharmonic contribution. An intrinsic temperature dependence of some vibrational frequencies appears to have been observed at 0 GPa [Gillet et al., 1991]. In Figure 5d, we show that \( \gamma_{th} \) at ambient conditions predicted by the QHA differs at most by 5% from those inferred from measurements with less thorough sampling of phonon frequencies [Chopelas, 1990; Gillet et al., 1991].

Table 4. Calculated Thermal Equation of State Compared With Experimental Data

<table>
<thead>
<tr>
<th>( T = 300 \text{ K} ), 0 GPa</th>
<th>( T = 300 \text{ K} ), 0 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation, This Study</td>
<td>Experiment</td>
</tr>
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<td>( V(\text{Å}^3) )</td>
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</tr>
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<td>( K_f \text{(GPa)} )</td>
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<td>( K_s \text{(GPa)} )</td>
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<td>( \alpha \times 10^{-3} \text{ K}^{-1} )</td>
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</tr>
<tr>
<td>( C_f\text{(J mol}^{-1} \text{ K}^{-1}) )</td>
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</tr>
<tr>
<td>( S\text{(J mol}^{-1} \text{ K}^{-1}) )</td>
<td>95.9</td>
</tr>
<tr>
<td>( \gamma_{th} \text{ (K}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}) )</td>
<td>1.23</td>
</tr>
<tr>
<td>( \gamma_m \text{ (K}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}) )</td>
<td>1.29</td>
</tr>
<tr>
<td>( K_s\text{(GPa)} )</td>
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</tr>
<tr>
<td>( \partial K_f / \partial T \times 10^{-2} \text{ GPa K}^{-1} )</td>
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<tr>
<td>( \partial K_s / \partial T \times 10^{-2} \text{ GPa K}^{-1} )</td>
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Figure 4. Calculated pressure-temperature-volume relations for forsterite. “Static” represents the results for static lattice (without zero point motion). “\( T = 0 \text{K}, \) with ZPM” represents the results after the zero point motion correction. “Exp a” represents the measured data in the temperature range 675–1273 K by Guyot et al. [1996]; “Cal a” is the calculated values at 300 K, 700 K, 1100 K, 1500 K, and 1900 K using QHA by Guyot et al. [1996]. “Exp b” represents the measured data in the temperature range 1019–1371 K by Meng et al. [1993]. Solid black lines are calculated results at P-T where QHA is valid; dashed lines extended beyond the solid are at P-T condition where QHA is invalid. (\( K_f \)) and adiabatic (\( K_s \)) bulk modulus are plotted in Figures 5a and b. Our \( K_f \) are in excellent agreement with experimental values at 0 GPa [Gillet et al., 1991] and so is \( K_s = K_f (1 + \alpha \gamma T) \) within the regime of validity of the QHA [Gillet et al., 1991; Isaak et al., 1989]. Figure 5c shows the thermal expansivity, \( \alpha = 1 / T (\partial V / \partial T)_P, \) which is determined from the volume dependence of temperature at each pressure. The scattering of experimental data [Bouhifd et al., 1996; Chopelas, 1990; Fei and Saxena, 1987; Gillet et al., 1991; Hazen, 1976; Kajiyoshi, 1986; Suzuki et al., 1984] is substantial at high temperatures even at 0 GPa. Nevertheless, our results are in very good
Figure 5. Calculated data at pressure ($P = 0, 2, 5, 10, 15, \text{ and } 20 \text{ GPa}$) and temperature ($T$). For Figures 5c–5h, the pressure is from 0 GPa to 20 GPa top-down. (a and b) Isothermal ($K_T$) and adiabatic bulk modulus ($K_S$); (c) thermal expansivity ($\alpha$), solid black lines are calculated results at P-T where QHA is valid; dashed lines extended beyond the solid are at P-T condition where QHA is invalid; (d) Grüneisen parameter ($\gamma$) compared with reported results [Gillet et al., 1991; Isaak et al., 1989]; (e and f) heat capacity $C_V$ and $C_P$ compared with reported results [Anderson, 1996; Gillet et al., 1991]; (g and h) entropy ($S$) versus $T$ and $P$, cross symbols are by Guyot et al. [1996]; square symbols are by Chopelas [1990].
A solid is said to be anharmonic in behavior when $C_V$ is larger than that predicted by the Dulong and Petit limit ($3nR$) [Cynn et al., 1996]. Forsterite demonstrates this behavior [Anderson, 1996; Cynn et al., 1996; Gillet et al., 1991] at zero pressure and high temperatures. The deviation of our calculated $C_V$ from the experimental results increases with temperature, particularly in the P-T regime where the QHA is no longer expected to be valid. This is the sign of anharmonic effects and is shown in Figure 5e. The difference between calculated and measured $C_p$, $C_p = C_V(1 + \alpha V T)$, is relatively small (Figure 5f). The temperature and pressure dependences of entropy are plotted in Figures 5g–5h. The negative pressure dependences of the entropy at all temperatures are consistent with the experimental results [Chopelas, 1990; Guyot et al., 1996].

Our calculated entropy agrees very nicely with the experimental estimates considering the limited number of phonon modes used in the experimental data.

5. Summary

We have reported first-principles phonon dispersion and vibrational density of states for Mg$_2$SiO$_4$ forsterite up to 20 GPa using density functional theory. Our calculated Raman and infrared frequencies and their pressure dependences are in excellent agreement with available experimental data. We also predict the pressure dependence of some modes which are yet to be measured. The thermoelastic properties were derived from calculated vibrational density of states (VDoS) in conjunction with the QHA. The calculated compression curves, the isothermal bulk modulus, and the constant pressure-specific heat and entropy agree extremely well with the reported experimental data, regardless of claimed anharmonic effects in this solid. The computed mode Gr"uneisen parameters, $\gamma_i$ at zero pressure for three modes, two $B_{3g}$ and one $B_{1u}$, differ considerably from measured values, pointing perhaps to the origin of anharmonic effects in this solid. However, the QHA still seems to be very effective in describing thermodynamic, including $C_V$, properties within its regime of validity. Deviations beyond this limit support the conclusion that forsterite is a solid that is both anharmonic in $C_V$ and quasi-harmonic in the thermal pressure in high-temperature region [Anderson, 1996; Cynn et al., 1996; Gillet et al., 1991]. The properties of this material at relevant mantle conditions are well predicted by the QHA.

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