Thermoelasticity of Fe\(^{2+}\)-bearing bridgmanite

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Abstract We present local density approximation augmented by the Hubbard-type correction calculations of high-temperature elastic properties of bridgmanite with composition (Mg\(_{1-x}\)Fe\(^{2+}\)\(_x\)Al\(_2\))\(_2\)SiO\(_4\) for 0 \(<\> x \leq 0.125\). Results of elastic moduli and acoustic velocities for the Mg end-member (x = 0) agree very well with the latest high-pressure and high-temperature experimental measurements. In the iron-bearing system, we focus particularly on the change in thermoelastic parameters across the state change that occurs in ferrous iron above ~30 GPa, often attributed to a high-spin (HS) to intermediate-spin (IS) crossover but explained by first-principles calculations as a lateral displacement of substitutional iron in the perovskite cage. We show that the measured effect of this change on the equation of state of this system can be explained by the lateral displacement of substitutional iron and not by the HS to IS crossover. The calculated elastic properties of (Mg\(_{0.875}\)Fe\(^{2+}\)\(_{0.125}\)SiO\(_4\)) along an adiabatic mantle geotherm somewhat overestimate longitudinal velocities but produce densities and shear velocities quite consistent with the Preliminary Reference Earth Model data throughout most of the lower mantle.

1. Introduction

Thermoelastic properties of lower mantle minerals provide a direct link to seismological observations. In order to constrain the composition and thermal structure of the Earth’s lower mantle, a detailed investigation of elastic properties of the constituent minerals is needed. Bridgmanite, (Mg,Fe,Al)(Si,Fe,Al)O\(_3\) perovskite (Pv), is the main constituent of the lower mantle along with (Mg,Fe)O ferropericlase, CaSiO\(_3\) perovskite, and (Mg,Fe,Al)(Si,Fe,Al)O\(_3\) postperovskite (PPv). Although there has been considerable progress in measurements of elastic properties of these minerals at high pressures and temperatures (Yeganeh-Haeri, 1994; Sinnelnikov et al., 1998; Fiquet et al., 2000; Andraut et al., 2001; Aizawa et al., 2004, 2005b; Sinogeikin et al., 2004; Li and Zhang, 2005; Murakami et al., 2007; Lundin et al., 2008; Boffa Ballaran et al., 2012; Chantel et al., 2012; Murakami et al., 2012; Dorfman et al., 2013), owing to extreme pressure and temperature conditions in the lower mantle, the availability of data on Fe-bearing bridgmanite is quite limited to well-constrained lower mantle composition and temperature. Several experiments and first-principles calculations have shown that pressure-induced iron spin crossover [Badro et al., 2003, 2004; Tsuchiya et al., 2006; Lin et al., 2012] affects elastic properties of (Mg,Fe)O ferropericlase (fp) [Goncharov et al., 2006; Crowhurst et al., 2008; Marquardt et al., 2009; Wentzcovitch et al., 2009; Wu et al., 2009; Antonangeli et al., 2011; Wu et al., 2013; Wu and Wentzcovitch, 2014]. In the case of iron-bearing bridgmanite, effects of spin crossover on elastic properties have been quite uncertain due to possible coexistence of ferrous (Fe\(^{2+}\)) and ferric (Fe\(^{3+}\)) iron along with the more complex perovskite crystal structure. Experimentally, it has been difficult to isolate the effects of ferrous and ferric iron unambiguously.

Acoustic velocity measurements using an ultrasonic technique [Chantel et al., 2012] and compression curve measurements [Boffa Ballaran et al., 2012] in iron-bearing bridgmanite demonstrated a significant change in bulk modulus across the state change in iron. By fitting experimental data with third-order Birch-Murnaghan equation of state to small (0–40 GPa) and large (0–75 GPa) pressure ranges, Boffa Ballaran et al. [2012] found ambient condition bulk modulus smaller (245 GPa) and larger (253 GPa), respectively. Since these fitting pressure ranges had no effect on the iron-free phase, Boffa Ballaran et al. [2012] attributed this behavior to change in compression mechanism caused by the high-spin (HS) to intermediate-spin (IS) crossover [McCammon et al., 2008]. However, the HS to IS crossover has not been found in first-principle
Figure 1. Pressure and temperature dependence of (a) elastic moduli and (b) sound velocities for \((\text{Mg}_1-x\text{Fe}_x\text{SiO}_3)\) with \(x = 0\) and 0.05 and of (c, d) \(dM/dx\) \((M = K_p, G, V_p, V_S)\). Solid (dashed) lines represent first-principles results within (outside) the validity of quasi-harmonic approximation. BS: Brillouin scattering, US: ultrasonic technique.

2. Method and Calculation Details

We have used density functional theory (DFT) \([Hohenberg and Kohn, 1964; Kohn and Sham, 1964]\) within the local density approximation (LDA) \([Ceperley and Alder, 1980]\) augmented by the Hubbard U (LDA + U) calculated self-consistently \([Cococcioni and de Gironcoli, 2005; Kulik et al., 2006; Hsu et al., 2009; Leiria Campo et al., 2014]\).
Table 1. Volume, Sound Velocities, Elastic Moduli, and Their Pressure Derivatives at Ambient Pressure and Temperature Conditions\(^a\)

| \(V\) (\(\text{Å}^3\)) | \(x\) | \(V_p\) (km/s) | \(V_s\) (km/s) | \(K_T\) (GPa) | \(G\) (GPa) | \(K'\) | \(G'\) | References |
|---|---|---|---|---|---|---|---|---|
| 163.2 | 0 | 10.72 | 6.42 | 242.5 | 168.2 | 3.96 | 1.79 | This study, single crystal/LDA |
| 163.3 | 0.05 | 10.63 | 6.34 | 245.8 | 167.02 | 4.03 | 1.79 | This study, single crystal/LDA+U (low QS) |
| 162.3 | 0 | 11.04 | 6.57 | 264(5) | 172(1) | - | - | Sinogeikin et al. [1998], polycrystal/US |
| 162.4(0.5) | 0 | 10.84(0.1) | 6.34 | 245.8 | 172(1) | - | - | Sinogeikin et al. [2004], polycrystal/BS |
| 166.5(0.2) | 0 | 11.04 | 6.46 | 236(2) | 174(1) | 4.7(0.1) | 1.56(0.04) | Sinogeikin et al. [2004], single crystal/BS |
| 162.3 | 0 | 10.66(0.05) | 6.54(0.04) | 253(3) | 173(3) | - | - | Chantel et al. [2012], single crystal/LDA+U |
| 162.4 | 0 | 10.88(0.05) | 6.47(0.06) | 253(3) | 173(3) | - | - | Chantel et al. [2012], polycrystal/US |
| 162.3 | 0 | 10.82(0.06) | 6.54(0.03) | 253(3) | 175(2) | - | - | Oganov et al. [2008], simulations |
| 162.3 | 0 | 10.86(0.05) | 6.49(0.04) | 253(3) | 173(1) | 4.4(0.1) | 2.0(0.1) | Li and Zhang [2005], polycrystal/US |
| - | 0 | 10.85(0.03) | 6.49(0.03) | - | 172(1.5) | - | 1.56(0.04) | Murakami et al. [2007], polycrystal/BS |
| 162.2(0.2) | 0 | 10.82(0.06) | 6.54(0.04) | 247(4) | 176(2) | 4.8(0.02) | 1.68(0.1) | Chantel et al. [2012], polycrystal/US |
| 166.5(0.2) | 0.05 | 10.60(0.06) | 6.46(0.04) | 236(2) | 174(1) | 4.7(0.1) | 1.56(0.05) | Chantel et al. [2012], polycrystal/US |
| 162.4 | 0 | - | - | 267 | 180 | 4.10 | - | Oganov et al. [2001], simulations |
| 162.49 | 0 | - | - | 269(2) | 159(2) | - | - | Marton and Cohen [2002], simulations |
| 162.4 | 0 | - | - | 250.5 | 172.9 | 4.01 | 1.74 | Zhang et al. [2013], simulations |

\(\text{Compression Studies}\)

| \(V\) (\(\text{Å}^3\)) | \(K_T\) | \(K'\) |
|---|---|---|
| 162.3 | 0 | 259(5) | 3.69 |
| 162.4 | 0 | 248.8 | 4 |
| 162.7 | 0.05 | 255.4 | 4 |
| 164.1 | 0 | 247 | 3.97 |
| 162.30 | 0 | 255–261 | 4 |
| 162.18 | 0.09 | 257–259 | 4 |
| 163.30 | 0.15 | 257–259 | 4 |
| 163.09(0.06) | 0.04 | 253(2) | 3.99(0.07) |
| 163.16(0.06) | 0.04 | 245(4) | 4.4(0.03) |
| 166.5(0.2) | 0.05 | 246(2) | 4 |
| 163.0 | 0.09 | 251(13) | 4 |

\(\text{BS}: \text{Brillouin scattering}; \text{US}: \text{ultrasonic}; \text{XRD}: \text{X-ray diffraction.}\)

\(^a\)BS: Brillouin scattering; US: ultrasonic; XRD: X-ray diffraction.

and Cococcioni, 2010; Himmetoglu et al., 2014]. Ultrasoft pseudopotentials [Vanderbilt, 1990] have been used for Fe, Si, and O. For Mg, a norm-conserving pseudopotential generated by von Barth-Car’s method has been used. A detailed description about pseudopotentials is available in Umemoto et al. [2008]. The plane wave kinetic energy and charge density cutoff are 40 Ry and 160 Ry, respectively. Structural optimization at arbitrary volumes has been performed using variable cell shape damped molecular dynamics [Wentzcovitch, 1991; Wentzcovitch et al., 1993]. Self-consistent and structurally consistent \(U_{\text{0}} = 3.1 \text{ eV}\), reported by Hsu et al. [2010] using the linear response approach [Cococcioni and de Gironcoli, 2005; Kulik et al., 2006], has been used for high-spin low-QS and high-QS iron. Vibrational density of states (VDoS), needed to calculate free energy within quasi-harmonic approximation [Carrier et al., 2007], have been calculated using density functional perturbation theory [Baroni et al., 2001] using the LDA + U functional [Floris et al., 2011]. (Mg\(_{1.25}\),Fe\(_{0.75}\))SiO\(_3\), for \(x = 0\) and 0.125 have been investigated in a 40-atom supercell. Elastic properties for \(0<x<0.125\) are linearly interpolated using \(x = 0\) and \(x = 0.125\) results. Electronic states have been sampled on a \(2 \times 2 \times 2\) Monkhorst-Pack \(k\)-point grid shifted by \((1/2, 1/2, 1/2)\) from the Brillouin zone origin. VDoS have been obtained by calculating dynamical matrices on a \(2 \times 2 \times 2\) \(q\)-point grid and interpolating the obtained force constants on an \(8 \times 8 \times 8\) \(q\)-point grid. The structure for \(x = 0\) and \(x = 0.125\) with high-QS state have been optimized at 12 pressures between \(-10\) and 150 GPa. The low-QS structure has been optimized up to 60 GPa only. Beyond this pressure unstable phonons appear. To obtain static elastic coefficients (zero temperature), \(C_{ij}\) at each pressure, positive and negative strains of 1% magnitude have been applied, and after relaxing the internal degrees of freedom, associated stresses have been calculated. Thermoelectric moduli have been calculated using a semianalytical approach [Wu and Wentzcovitch, 2011]. This method uses an analytical expression for strain Grüneisen parameters to calculate the thermal contribution to
3. Results and Discussion

3.1. Elasticity of Iron-Free and Fe$^{2+}$-Bearing Bridgmanite

The calculated aggregate elastic moduli, $K$ and $G$, and acoustic velocities, $V_P$ and $V_S$, of iron-free bridgmanite compare well with Brillouin scattering measurements of Murakami et al. (2007, 2012) as shown in Figures 1a and 1b. Within experimental uncertainties, ultrasonic measurements of Li and Zhang (2005) and Chantel et al. (2012) also compare well with our results. Table 1 compares calculated elastic properties at zero pressure and 300 K with measurements and simulations at ambient conditions. As compared to experimental measurements, our calculated volume is overestimated by $\sim$0.5%, while elastic moduli and acoustic velocities are underestimated by $\sim$1–3%, which is typical for LDA calculations after including zero-point energy [Karki et al., 1999, 2001; Wentzcovitch et al., 2004, 2010a, 2011b]. Calculated pressure derivatives of elastic moduli, $K'$ and $G'$, are 3.96 and 1.79, respectively. Our $K'$ agrees reasonably well with previous studies, while $G'$ compares well with those reported by Sinnelnikov et al. [1998] and Zhang et al. [2013]. Comparing acoustic velocities and elastic moduli at higher temperatures, especially shear velocities and shear moduli at 2700 K by Murakami et al. (2012), we find that the temperature dependence of elastic properties has been captured well. As shown in Figure 2, our calculated $\frac{dK}{dT}$ and $\frac{dG}{dT}$ are smaller in magnitude compared to values obtained by ultrasonic [Sinnelnikov et al., 1998; Aizawa et al., 2004; Li and Zhang, 2005] at 0 GPa and Brillouin scattering measurements [Chantel et al., 2012] at 22 GPa. Calculated values of $\frac{dK}{dT}$ compare well with those of previous calculations [Oganov et al., 2001; Marton and Cohen, 2002; Wentzcovitch et al., 2004; Zhang et al., 2013]. Calculated $\frac{dG}{dT}$ agree well with Brillouin scattering measurements by Murakami et al. (2012) and nonself-consistent calculation by Marton and Cohen [2002] but differ substantially from that of Oganov et al. [2001], Wentzcovitch et al. [2004], and Zhang et al. [2013].

The semianalytical method used here had produced well the temperature dependence of elasticity for all applied materials [Wu and Wentzcovitch, 2011; Nunez-Valdez et al., 2012a, 2012b, 2013; Yang and Wu, 2014].
This method has also produced slightly better results for MgO [Wu and Wentzcovitch, 2011] than the fully numerical method [Karki et al., 1999; Wentzcovitch et al., 2004]. This is because this method avoids calculations of vibrational frequencies in strained configurations and numerical errors associated with finite difference calculations of elastic coefficients.

The elastic moduli and acoustic velocities of iron-bearing bridgmanite at lower mantle pressures are also shown in Figure 1. To compare with measurements of Boffa Ballaran et al. [2012] and Chantel et al. [2012] in the iron-bearing phase, we estimated elastic properties for $0 < x < 0.125$ by linearly interpolating the calculated results for $x = 0$ and $x = 0.125$. The calculated volume at ambient conditions is in agreement with measurements by Boffa Ballaran et al. [2012] for $x = 0.04$ and is smaller by $\sim 2\%$ when compared with measurements by Chantel et al. [2012] for $x = 0.05$ (Table 1). As shown in Figure 1b, comparison of calculated acoustic velocities, $V_P$ and $V_S$, for $x = 0.05$ with the only available experimental measurements for $(Mg_{0.95}Fe^{2+}_{0.04}Fe^{3+}_{0.01})SiO_3$ [Chantel et al., 2012] is also good except for the shear velocity data in the lower pressure range. As seen in Figures 1c and 1d and in Table 1, the presence of iron has very little to no effect on bulk modulus, $K_S$, but shear modulus $G$ softens by $\sim 2$ to $6\%$, consistent with previous static first-principles studies [Kiefer et al., 2002; Lundin et al., 2008]. The effect of iron on the temperature dependence of acoustic velocities and elastic moduli is not very significant (see Figure 1).

### 3.2. Effect of Pressure-Induced Iron Displacement on Elasticity

We have investigated the elastic consequences of the pressure-induced iron displacement [Hsu et al., 2010; Hsu and Wentzcovitch, 2014] by calculating thermal elastic moduli and acoustic velocities for $x = 0.125$ with iron in low-QS and high-QS sites. The low-QS structure is stable up to 60 GPa in LDA+U calculations. Above this pressure unstable phonon modes start appearing. As shown in Figure 3, vibrational density of states (VDoS) for $x = 0$ and for $x = 0.125$ with iron in the high-QS and low-QS sites are not very different except for a small shift toward lower frequencies owing to the presence of iron. However, there is an extra peak at $\sim 150 \, \text{cm}^{-1}$ in the VDoS if iron is in the low-QS site. It is worth noting that the vibrational mode associated with this extra peak in the low-QS structure is infrared active, while the same mode is infrared inactive in the high-QS structure. This information may provide a crucial test to investigate the states of ferrous iron in bridgmanite.

The effect of iron displacement (low-QS to high-QS transition) on unit-cell volume, acoustic velocities, and elastic moduli of iron-bearing bridgmanite with $x = 0.125$ is shown in Figure 4. To quantify the magnitude of the property change, we define the contrast $\Delta$ in a particular property $M$ as...
Table 2. Calculated Equation of State Parameters for Low QS, High QS, and Combined Results at 30 GPa for Low QS and High QS Fitted With Different Pressure Range

|                   | 300 K     | 700 K     |
|-------------------|-----------|-----------|
|                   | V (Å³)    | Kₚ        | K'ₚ     |
| Low QS            | 163.81    | 247.16    | 4.05    |
|                   | 165.62    | 234.05    | 4.12    |
| High QS           | 163.64    | 248.90    | 3.97    |
|                   | 165.44    | 236.44    | 4.03    |
| Combined data (0–150 GPa) | 163.81    | 245.59    | 4.02    |
|                   | 165.62    | 233.93    | 4.06    |
| Combined data (0–90 GPa) | 163.87    | 243.41    | 4.09    |
|                   | 165.67    | 232.32    | 4.11    |
| Combined data (0–75 GPa) | 163.93    | 241.25    | 4.15    |
|                   | 165.68    | 232.29    | 4.12    |

ΔM = \frac{M_{\text{high-QS}} - M_{\text{low-QS}}}{M_{\text{low-QS}}} × 100. As shown in Figure 4, the volume contrast is very small (~0.1%), consistent with Lundin et al. [2008] and Boffa Ballaran et al. [2012], and is unlikely to be detected in experiments. The contrast in bulk modulus, Kₛ, and acoustic velocities, Vₛ and Vₚ, are also small. However, the shear modulus contrast is about ~0.5–1.5%. This change in G was also suggested by Boffa Ballaran et al. [2012] using spontaneous strain analysis. To investigate the fitting pressure-range behavior observed by Boffa Ballaran et al. [2012] and Chantel et al. [2012], the calculated results for low QS and high QS have been combined at 30 GPa, the pressure above which the HS to IS crossover was proposed by McCammon et al. [2008] and Potapkin et al. [2013]. The third-order Birch-Murnaghan equation of state was used to fit these combined results. As shown in Table 2, depending on the pressure range of the combined results, an isothermal bulk modulus softening of ~3 to 7 GPa has been found. This softening, however, reduces with increasing temperature.

Intermediate-spin (IS) states of the iron in Fe²⁺-bearing bridgmanite are energetically unfavored in the lower mantle pressure range [Hsu et al., 2010; Hsu and Wentzcovitch, 2014], and phonon calculations have been extremely difficult for these states. To understand the overall trend of fitting parameters of combined low-QS and IS data, we have used static data for low-QS state and IS state with QS value 0.9–1.6 mm/s [Hsu and Wentzcovitch, 2014]. The static bulk modulus at zero pressure for low-QS and IS states are 263.2 GPa and 254.1 GPa, respectively (Figure S3 in the supporting information). When static low-QS and IS results have been combined at 30 GPa and fitted within different pressure ranges of 0–150 GPa and 0–120 GPa, static bulk modulus of the combined fit are 305 GPa and 348.7 GPa, respectively (Figure S4). The fitting pressure-range trend of combined low QS and high QS is the same as that observed by Boffa Ballaran et al. [2012] and Chantel et al. [2012], while of combined low-QS and IS states the fitting trend is opposite. These findings substantiate our understanding that ferrous iron in perovskite remains in the HS state in the lower mantle pressure range and instead undergoes a horizontal displacement in the perovskite cage which results in an increase in Mössbauer quadrupole splitting.

4. Geophysical Significance

As shown in Figure 5, elastic moduli (Kₛ, G), acoustic velocities (Vₚ, Vₛ), and densities (ρ) are calculated along the Boehler’s geotherm [Boehler, 2000] using new [Wu and Wentzcovitch, 2011] and previous [Karki et al., 1999; Wentzcovitch et al., 2004] methods, and the results are compared with seismic values from the Preliminary Reference Earth Model (PREM) [Dziewonski and Anderson, 1981]. Owing to the smaller magnitude of \frac{\partial G}{\partial T} obtained here, present results for G and Vₛ differ more from previous results by Wentzcovitch et al. [2004] in the deep lower mantle region, where temperatures are higher. This difference is sufficient to alter conclusions regarding mantle composition. Inclusion of 12.5% Fe²⁺ in MgSiO₃ perovskite produces good agreement of ρ, Vₛ, and G with PREM values (Figures 5c and 5d). Therefore, comparison of calculated Vₛ with PREM’s Vₛ may indeed suggest a more perovskitic lower mantle [Murakami et al., 2012]. However, relatively large values of Kₛ and Vₛ are found, suggesting that the lower mantle may accommodate a reasonable amount of ferropericlase, (MgFe)O, and CaSiO₃ perovskite as previously indicated [Wentzcovitch et al., 2004]. Resolving whether the lower mantle composition is pyrolytic or perovskitic still needs more detailed investigations of the effect of Al₂O₃ and Fe₂O₃ on the elasticity of bridgmanite along with the elasticity of CaSiO₃ perovskite. Ultimately, the analysis of one-dimensional velocity profiles might be too limited to address this question more conclusively. Analysis of lateral heterogeneities, including effects of...
This study

Wentzcovitch et al. [2004]

PREM

Figure 5. Elastic moduli ($K_S, G$), sound velocities ($V_P, V_S$), and density ($\rho$) for ($\text{Mg}_1-x\text{Fe}_x\text{SiO}_3$) with (a, b) $x=0$ and (c, d) $x=0.125$ calculated along the Boehler's geotherm [Boehler, 2000] using present [Wu and Wentzcovitch, 2011] and previous [Wentzcovitch et al., 2004] methods.

5. Conclusions

We have presented first-principles LDA + U calculations of aggregate elastic moduli and acoustic velocities for Fe$^{2+}$-bearing bridgmanite at lower mantle conditions. Using the new semianalytical approach for high-temperature elasticity [Wu and Wentzcovitch, 2011], we find an unexpected difference of temperature gradients with respect to previous fully numerical calculations [Wentzcovitch et al., 2004] also based on the quasi-harmonic approximation. New results for $\frac{dG}{dT}$ and $\frac{dV_S}{dT}$ for iron-free bridgmanite are in good agreement with the latest high-temperature high-pressure measurements of these quantities by Murakami et al. [2012], which also differ from previous calculations and previous experiments. Overall, it appears that pressure and temperature gradients of bulk and shear moduli are better estimated now. Calculated acoustic velocities for iron-bearing bridgmanite also agree well with ultrasonic measurements of Chantel et al. [2012].

We do not find any significant effect of iron-site change (low QS to high QS) on sound velocities and elastic moduli, except for $\sim$1% increase in shear modulus, consistent with findings by Boffa Ballaran et al. [2012]. Effects of fitting combined data for low-QS and high-QS states on elastic properties are consistent with fitting pressure-range behavior previously observed by Boffa Ballaran et al. [2012] and Chantel et al. [2012].

Calculated shear modulus and shear velocities of bridgmanite along a typical mantle geotherm are qualitatively more consistent with PREM values now compared with previous first-principles results [Wentzcovitch et al., 2004]. Differences in bulk modulus and longitudinal velocities remain noticeable.
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