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# Elasticity of (Mg,Fe)$SiO_3$-Perovskite at high pressures

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[1] We calculated the elasticity of (Mg,Fe)$SiO_3$-perovskite, using the plane-wave pseudopotential method for a pressure range that encompasses the earth's lower mantle. Adding 25 mol% $FeSiO_3$ to the Mg endmember decreases the shear modulus by 6% at zero pressure and by 8% at core mantle boundary pressures. The bulk modulus is less affected by iron, increasing by 2% at zero pressure and by 1% at the base of the mantle. For the isotropically averaged wave velocities we find that the compressional wave velocity decreases by 4% independent of pressure and the shear wave velocity decreases by 6% and 7% at zero pressure and at 136 GPa, repectively. For the relative variation of shear to compressional velocities at constant pressure due to variations in Fe-content we find $R$ = 1.6 at 136 GPa and for the relative variation of shear to bulk sound velocities we find $\xi$ = 2.6 at 136 GPa. *INDEX TERMS:* 3919 Mineral Physics: Equations of state; 3924 Mineral Physics: High-pressure behavior; 3909 Mineral Physics: Elasticity and anelasticity; 7207 Seismology: Core and mantle

## 1. Introduction

[2] It is thought that $(Mg_{1-x},Fe_x)SiO_3$-perovskite is the most abundant mineral in the earth's lower mantle and its elastic properties are important for the formulation of compositional models of this largest single region within the earth. Previous experimental studies have largely focused on the equation of state of $MgSiO_3$-perovskite [*Fiquet et al.*, 2000; *Shim et al.*, 2001] at lower mantle conditions. The elastic constants of the Mg end-member have been measured at ambient conditions from Brillouin scattering experiments [*Yeganeh-Haeri*, 1994] and the shear modulus has been determined up to 800 K from ultrasonic measurements [*Sinelnikov et al.*, 1998]. The pressure dependence of the elastic constants has been predicted for $x$ = 0 at static conditions [*Karki et al.*, 1997; *Wentzcovitch et al.*, 1998] and at high temperatures [*Oganov et al.*, 2001a, 2001b]. Still less is known about elastic properties of ferromagnesian silicate perovskite. The effect of iron on the zero pressure volume has been determined experimentally [*Knittle et al.*, 1986; *Kudoh et al.*, 1990; *Parise et al.*, 1990; *Jephcoat et al.*, 1999] and up to 30 GPa and 900 K [*Mao et al.*, 1991]; only one study was done at higher pressures [*Knittle and Jeanloz*, 1987]. The effect of iron on elastic properties, especially the shear modulus is unknown.

[3] We have determined the equation of state and all nine elastic constants of $(Mg_{0.75},Fe_{0.25})SiO_3$-perovskite up to 140 GPa which encompasses the pressure range of the lower mantle. From the elastic constants we determine the seismic wave velocities and discuss possible implications for lower mantle mineralogy.


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## 2. Theory

[4] The first-principles method combines symmetry preserving, variable cell-shape relaxation and density functional theory. This approach has been applied successfully to obtain elastic properties of earth materials [*Kiefer et al.*, 1997; *Karki et al.*, 2001]. Computations were performed with VASP [*Kresse and Hafner*, 1993; *Kresse and Furthmüller*, 1996a, 1996b]. Two approximations are made: First, the electronic exchange and correlation is described within the local density approximation (LDA) [*Ceperley and Alder*, 1980]. We also performed alternate calculations within the generalized gradient approximation (GGA) [*Perdew*, 1991]. Second, ultrasoft pseudopotentials are used [*Vanderbilt*, 1990; *Kresse and Hafner*, 1994] for Mg, Fe, Si, and O with $R_c$ = 2.000 Bohr, $R_c$ = 1.701 Bohr, $R_c$ = 1.800 Bohr, $R_c$ = 1.550 Bohr for the core radii of the local potential, respectively. The cell shape and all internal structural parameters were optimized simultaneously at static (0 K) conditions using a conjugate gradient scheme. The calculations are spin polarized to account for the magnetism of iron. We fixed iron in its high spin state, which has been indicated by all electron calculations to be the stable electronic configuration throughout the pressure range of the lower mantle for $FeSiO_3$-perovskite [*Cohen et al.*, 1997].

[5] (Mg,Fe)$SiO_3$-perovskite belongs to the spacegroup *Pbnm* [*Horiuchi et al.*, 1987; *Kudoh et al.*, 1990] with four (Mg,Fe)$SiO_3$ units per unit cell. Tests showed that fully converged solutions of the Kohn-Sham equations were obtained by including plane waves up to a kinetic energy cut-off of $E_{cut}$ = 600 eV and a 2 × 2 × 2 Monkhorst-Pack grid [*Monkhorst and Pack*, 1976]. These parameters were adopted for all calculations presented here and lead to total energies that are converged to within 0.6 meV/atom and Pulay stresses that are lower than 0.05 GPa.

[6] We consider substitutions of the type Fe → Mg on the large (4c) site which is thought to be the dominant mechanism to incorporate iron into perovskite in the absence of coupled substitutions [*Cohen et al.*, 1997]. We place a Fe atom on one of the symmetrically equivalent large sites in a 20 atom unit cell, corresponding to x = 0.25. To determine the elastic constants, the equilibrium structure was strained, and the internal parameters were re-relaxed. To obtain accurate elastic constants in the limit of zero strain, we applied small positive and negative strains of magnitude 1%.

[7] Experiments show that Fe substitution leaves the space group symmetry unaffected, indicating a disordered Mg-Fe arrangement. In contrast, the computed elastic constants are for a non-isotropic Mg-Fe arrangement of lowered (monoclinic) symmetry. We account for disorder by averaging over the possible symmetrically equivalent positions of the Fe atom:

$$C_{ijkl} = \frac{1}{4}\sum_{s=1}^{4} R^s_{im} R^s_{jn} R^s_{ko} R^s_{lp} \tilde{C}_{mnop} \qquad (1)$$

where $\tilde{C}$ are the computed elastic constants, and the $R^s$ are the rotational portion of the space group operations that relate the four symmetrically equivalent 4c sites to one another (including the

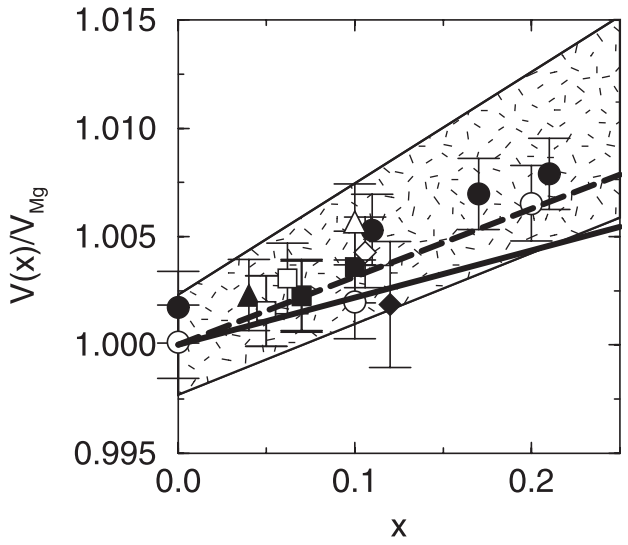


**Figure 1.** Effect of iron on the zero pressure volume of $(Mg_{1-x}, Fe_x)SiO_3$-perovskite. Solid line: LDA; dashed line: GGA. All experimental data are normalized to the value for the Mg endmember $V_{Mg} = 24.46$ cm$^3$/mol from *Jeanloz and Thompson* [1983]. Shaded area: Range of $V(x)$ as obtained by *Jeanloz and Thompson* [1983]. Filled circle: *Yagi et al.* [1979]; filled square: *Ito and Yamada* [1982]; filled diamond: *Knittle and Jeanloz* [1987]; filled triangle: *Kudoh et al.* [1990]; open circle *Mao et al.* [1991]; open square: *Jephcoat et al.* [1999]; open diamond: *Parise et al.* [1990], and open triangle: *O'Neill and Jeanloz* [1994].

identity). The resulting averaged elastic constants, $C$, have the appropriate orthorhombic symmetry. Below we report only values of $C$ from our static (0 K) calculations.

## 3. Results

[8] We find that the volume increases with increasing iron content at a rate that is consistent with most experimental data (Figure 1). Notable exceptions include the most iron-rich point of *Mao et al.* [1991], and the data of *Yagi et al.* [1979] which are systematically shifted to larger volumes. However, the trend defined by the Yagi et al. data agrees well with the LDA prediction. LDA predicts the static zero pressure volume for $x = 0$, $V(0)$, to be 1.7% smaller than the experimental value at ambient conditions, essentially identical to the difference expected from thermal effects. In contrast, GGA overestimates the volume: $V(0)$ is 4.2% larger than the experimental value; the addition of thermal contributions would increase the discrepancy between GGA and experiment. Underbinding is a common feature of GGA calculations of silicates and oxides and leads also to underestimated elastic constants (Table 1). The elastic constants for $x = 0$ as obtained from our LDA calculations agree favorably with previous first-principles calculations, except those of *Oganov et al.* [2001b] which are substantially lower as expected of GGA calculations. Our calculations also agree well with Brillouin scattering data [*Yeganeh-Haeri*, 1994] to within 5% for most elastic constants. The only exception is $C_{12}$ which agrees to within 3% between the different LDA calculations but is 10% smaller than the experimental value (Table 1). For $x = 0.25$ we find that the relative magnitude of the elastic constants remains the same as for $x = 0$. The largest change occur for $C_{66}$ which decreases by 12% and for the off-diagonal elastic constants which increase by 10%, 7% and 8% for $C_{12}$, $C_{13}$ and $C_{23}$, respectively.

[9] We calculated the isotropically averaged bulk and shear moduli, and the compressional and shear wave velocities within the Voigt-Reuss-Hill averaging scheme (Figure 2). Upon Fe substitution, the bulk modulus increases by 2% at zero pressure and 1% at 136 GPa, for $x = 0.25$. These small changes may be difficult to detect in equation of state measurements and fall within the experimental uncertainties for the bulk modulus of ≈2% [*Jeanloz and Thompson*, 1983; *Mao et al.*, 1991; *Fiquet et al.*, 1998]. In contrast, the effect of iron on the shear modulus is more pronounced and increases with pressure, at zero pressure the shear modulus decreases by 6% and at core mantle boundary pressures it decreases by 8%. The calculated isotropic velocities decrease at zero pressure by 4% and 6% for compressional ($V_P$) and shear waves ($V_S$), respectively. Changes in $V_P$ are almost pressure independent while $V_S$ is affected somewhat more strongly by Fe-substitution at high pressures: reduction by 7% at 136 GPa (Figure 2). To describe the dependence of bulk and shear moduli on iron content we adopt a linear relationship [*Jeanloz and Thompson*, 1983]:

$$M(x) = M_0(1 + b_M x) \tag{2}$$

where $M = K, G$. For $b_K$ we find 0.079 and 0.044 and for $b_G$ we find −0.22 and −0.31 at zero pressure and 136 GPa, respectively.

**Table 1.** Comparison of elastic moduli, $M_0$ (GPa), their pressure derivatives, $M_0'(-)$, elastic wave velocities (km s$^{-1}$) and their pressure derivatives (in km s$^{-1}$ GPa$^{-1}$) as determined from theory and experiment for $(Mg_{1-x}, Fe_x)SiO_3$-Perovskite at zero pressure

| | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ | $K$ | $G$ | $V_P$ | $V_S$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_0$[a] | 491 | 554 | 474 | 203 | 176 | 153 | 134 | 139 | 152 | 263 | 178 | 10.94 | 6.53 |
| $M_0'$[a] | 5.12 | 6.49 | 7.09 | 1.86 | 1.27 | 2.03 | 3.70 | 2.55 | 2.75 | 4.06 | 1.70 | 0.048 | 0.019 |
| $M_0$[b] | 488 | 543 | 469 | 193 | 173 | 135 | 147 | 148 | 164 | 268 | 168 | 10.48 | 6.13 |
| $M_0'$[b] | 5.24 | 6.27 | 7.00 | 1.75 | 1.17 | 1.69 | 3.79 | 2.60 | 2.85 | 4.10 | 1.57 | 0.046 | 0.017 |
| $M_0$[c] | 485 | 560 | 473 | 200 | 176 | 155 | 130 | 136 | 144 | 259 | 179 | – | – |
| $M_0$[d] | 487 | 524 | 456 | 203 | 186 | 145 | 128 | 144 | 156 | 258 | 175 | 10.94 | 6.53 |
| $M_0$[e] | 444 | 489 | 408 | 194 | 172 | 131 | 110 | 126 | 136 | 231 | 162 | 10.64 | 6.41 |
| $M_0$[f] | 482 | 537 | 485 | 204 | 186 | 147 | 144 | 147 | 146 | 264 | 177;175[g] | 11.04 | 6.57;6.56[g] |

The pressure dependence of the elastic constants was obtained from third order eulerian strain fits [*Davies*, 1974] to the calculated elastic constants. Isotropic bulk ($K$) and shear moduli ($G$) and elastic velocities ($V_P$ and $V_S$) were calculated asVoigt-Reuss-Hill averages.

[a] This work, $x = 0$.

[b] This work, $x = 0.25$.

Previous theoretical and experimental work for $x = 0$:

[c] *Wentzcovitch et al.* [1998].

[d] *Karki et al.* [1997].

[e] *Oganov et al.* [2001b].

[f] Brillouin scattering data from *Yeganeh-Haeri* [1994].

[g] Ultrasonic measurements *Sinelnikov et al.* [1998].

The values for $K_0$ and $K_0'$ are consistent with the values derived from the equation of state $V_0 = 159.6$ Å$^3$, $K_0 = 264.3$ GPa, $K_0' = 3.94$ and $V_0 = 160.5$ Å$^3$, $K_0 = 270.0$ GPa, $K_0' = 3.96$ for $x = 0$ and $x = 0.25$, repectively.

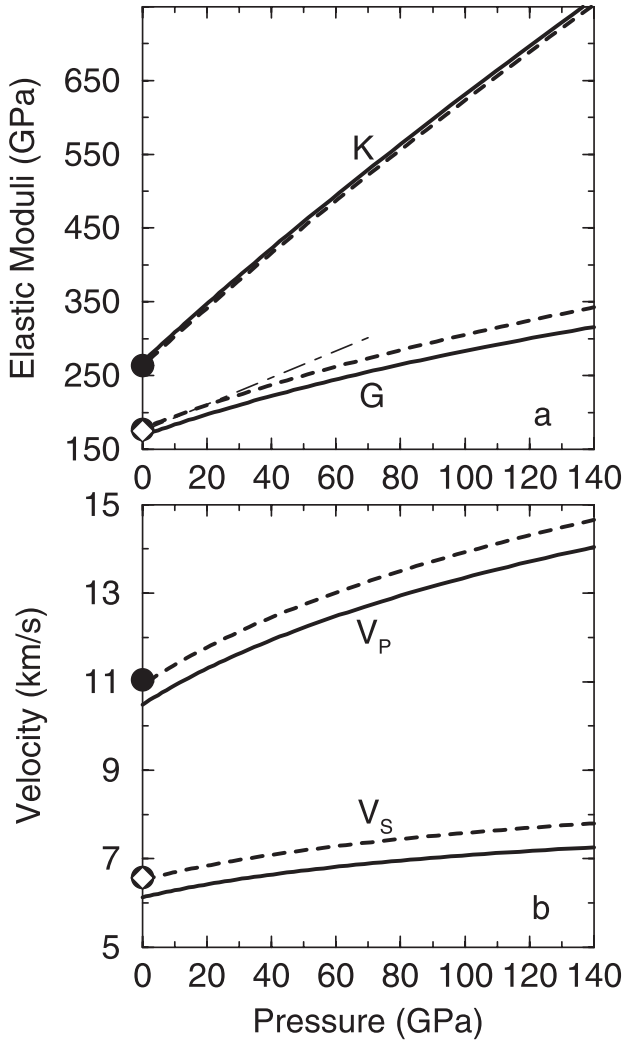


**Figure 2.** Voigt-Reuss-Hill averages of the elastic moduli and the elastic velocities. (a) Bulk modulus ($K$) and shear modulus ($G$). Solid lines: $x = 0.25$, dashed lines: $x = 0$. Solid circles: experimental data from Brillouin scattering [*Yeganeh-Haeri*, 1994]; open diamond and dot-dashed line, at zero pressure from ultrasonic measurements [*Sinelnikov et al.*, 1998]. (b) Compressional ($V_P$) and shear ($V_S$) velocity. Solid lines: $x = 0.25$, dotted lines: $x = 0$. Solid circles: Brillouin scattering data [*Yeganeh-Haeri*, 1994]; open diamond, shear modulus and initial slope $\partial G/\partial P$ at zero pressure from ultrasonic measurements [*Sinelnikov et al.*, 1998]. All experimental data are for the Mg end-member.

The dependence of the shear modulus on iron content is similar to that found experimentally for orthopyroxene ($b_G = -0.31$, *Duffy and Anderson* [1989]).

## 4. Discussion and Conclusions

[10] Seismic tomography provides snapshots of the earth's interior in terms of observed lateral velocity variations. The causes for these variations are manifold and may include variations in temperature, phase, and composition. In order to evaluate the effect of lateral variations in Fe-content we calculated the relative variations of compressional ($V_P$), shear ($V_S$) and bulk sound ($V_B$) velocities

$$R = \frac{\partial \ln V_S}{\partial \ln V_P} \quad \text{and} \quad \xi = \frac{\partial \ln V_S}{\partial \ln V_B}. \tag{3}$$

We find that $R$ and $\xi$ increase slightly with pressure and we obtain (LDA) 1.46 and 1.62 for $R$ and 0.41 and 0.39 for $\xi$ at 0 GPa and 136 GPa, respectively. The ratios as obtained from the GGA calculations are similiar. These values are much smaller as compared to the $R$ in excess of 3, as observed in seismic tomography for the deep lower mantle [*Masters et al.*, 2000]. This indicates that lateral variations of Fe content in (Mg,Fe)$SiO_3$-perovskite alone can neither account for the observed high values of $R$ nor for an anti-correlation of $V_S$ and $V_B$.

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