Elasticity of (Mg,Fe)SiO3-Perovskite at high pressures

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Received 7 January 2002; revised 27 March 2002; accepted 28 March 2002; published June 2002.

1. Introduction

It is thought that (Mg1-x,Fe)xSiO3-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 MgSiO3-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 [Vegnan-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.

We have determined the equation of state and all nine elastic constants of (Mg0.75,Fe0.25)SiO3-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.

2. Theory

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* = 2.000 Bohr, R* = 1.701 Bohr, R* = 1.800 Bohr, R* = 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 FeSiO3-perovskite [Cohen et al., 1997].

(Mg,Fe)SiO3-perovskite belongs to the spacegroup Pbnm [Horiuchi et al., 1987; Kudoh et al., 1990] with four (Mg, Fe)SiO3 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 Ecum = 600 eV and a 2 x 2 x 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.

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%.

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:

\[ C_{ijkl} = \frac{1}{4} \sum_{x=1}^{4} R^x_{ik} R^x_{jl} R^x_{il} R^x_{jk} \bar{C} \]

where \( \bar{C} \) are the computed elastic constants, and the \( R^x \) 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 (Mg₁₋ₓ, Feₓ)SiO₃-perovskite. Solid line: LDA; dashed line: GGA. All experimental data are normalized to the value for the Mg endmember \( V_{0} \). Shaded area: Range of \( V(0) \) as obtained by Jeanloz and Thompson [1983]. Filled circle: Yagi et al. [1979]; filled square: Ito and Yamaeda [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: Purise et al. [1990], and open triangle: O’Neill and Jeanloz [1994].

### 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

\( M(x) = M_{0}(1 + b_{M} x) \)  

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, \( M_{0}'(\cdot) \), elastic wave velocities (km s⁻¹) and their pressure derivatives (in km s⁻¹ GPa⁻¹) as determined from theory and experiment for (Mg₁₋ₓ, Feₓ)SiO₃-perovskite at zero pressure

<table>
<thead>
<tr>
<th>( C_{11} )</th>
<th>( C_{22} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>( C_{55} )</th>
<th>( C_{66} )</th>
<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{23} )</th>
<th>( K )</th>
<th>( G )</th>
<th>( V_{P} )</th>
<th>( V_{S} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{0} )</td>
<td>491</td>
<td>540</td>
<td>474</td>
<td>203</td>
<td>176</td>
<td>153</td>
<td>134</td>
<td>139</td>
<td>152</td>
<td>263</td>
<td>178</td>
<td>10.94</td>
</tr>
<tr>
<td>( M_{0}' )</td>
<td>5.12</td>
<td>6.49</td>
<td>7.09</td>
<td>1.86</td>
<td>1.27</td>
<td>2.03</td>
<td>3.70</td>
<td>2.55</td>
<td>2.75</td>
<td>4.06</td>
<td>1.70</td>
<td>0.048</td>
</tr>
<tr>
<td>( M_{0} )</td>
<td>488</td>
<td>543</td>
<td>469</td>
<td>193</td>
<td>173</td>
<td>135</td>
<td>147</td>
<td>148</td>
<td>164</td>
<td>268</td>
<td>168</td>
<td>10.48</td>
</tr>
<tr>
<td>( M_{0}' )</td>
<td>5.24</td>
<td>6.27</td>
<td>7.00</td>
<td>1.75</td>
<td>1.75</td>
<td>1.69</td>
<td>3.79</td>
<td>2.60</td>
<td>2.85</td>
<td>4.10</td>
<td>1.57</td>
<td>0.046</td>
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<tr>
<td>( M_{0} )</td>
<td>485</td>
<td>560</td>
<td>473</td>
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<td>176</td>
<td>155</td>
<td>130</td>
<td>136</td>
<td>144</td>
<td>252</td>
<td>129</td>
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<td>( M_{0}' )</td>
<td>487</td>
<td>524</td>
<td>456</td>
<td>203</td>
<td>186</td>
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<td>258</td>
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<td>( M_{0} )</td>
<td>444</td>
<td>489</td>
<td>408</td>
<td>194</td>
<td>172</td>
<td>131</td>
<td>110</td>
<td>126</td>
<td>136</td>
<td>231</td>
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<td>10.64</td>
</tr>
<tr>
<td>( M_{0}' )</td>
<td>482</td>
<td>537</td>
<td>485</td>
<td>204</td>
<td>186</td>
<td>147</td>
<td>144</td>
<td>147</td>
<td>146</td>
<td>264</td>
<td>177</td>
<td>6.57</td>
</tr>
</tbody>
</table>

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 as Voigt-Reuss-Hill averages.

* This work, \( x = 0 \).
* This work, \( x = 0.25 \).

Previous theoretical and experimental work for \( x = 0 \): * Wentzcowich et al. [1998].
* Karki et al. [1997].
* Oganov et al. [2001b].
* Brillouin scattering data from Yeganeh-Haeri [1994].

The values for \( K_{0} \) and \( K_{0}' \) are consistent with the values derived from the equation of state \( V_{0} = 159.6 \text{ Å}^{3}, K_{0} = 264.3 \text{ GPa}, K_{0}' = 3.94 \) and \( V_{0} = 160.5 \text{ Å}^{3}, K_{0} = 270.0 \text{ GPa}, K_{0}' = 3.96 \) for \( x = 0 \) and \( x = 0.25 \), respectively.
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 similar. 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 cannot neither account for the observed high values of $R$ nor for an anti-correlation of $V_S$ and $V_B$.

[11] Acknowledgments. This work was supported by the National Science Foundation under grants EAR-9973139 (LPB) and EAR-9973130 (RMW).

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[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

\begin{equation}
R = \frac{\partial \ln V_S}{\partial \ln V_P} \quad \text{and} \quad \xi = \frac{\partial \ln V_S}{\partial \ln V_B}
\end{equation}

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

4. Discussion and Conclusions

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

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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 [Veganeh-Haeri, 1994]; open diamond and dot-dashed line, at zero pressure from ultrasonic measurements [Sinelhnikov 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 [Veganeh-Haeri, 1994]; open diamond, shear modulus and initial slope $\partial G/\partial P$ at zero pressure from ultrasonic measurements [Sinelhnikov et al., 1998]. All experimental data are for the Mg end-member.

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 similar. 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 cannot neither account for the observed high values of $R$ nor for an anti-correlation of $V_S$ and $V_B$.

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