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

B. Kiefer and L. Stixrude
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA

R. M. Wentzcovitch
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, USA
Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste, Italy

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1. Introduction

It is thought that (Mg,Fe)SiO3-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 endmember 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.

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 Rₚ = 2.000 Bohr, Rₛ = 1.701 Bohr, Rₒ = 1.800 Bohr, Rₛ = 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 E_k = 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.

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 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:

\[
C_{ijkl} = \frac{1}{4} \sum_{s=1}^{4} R_{js}^s R_{ks}^s R_{ls}^s C_\text{mp}
\]  

where \(\dot{C}\) 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 \((\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3\)-perovskite. Solid line: LDA; dashed line: GGA. All experimental data are normalized to the value for the Mg endmember \(V_{00} = 24.46 \text{ cm}^3/\text{mol}\) from Jeanloz and Thompson [1983]. Shaded area: Range of \(V(x)\) as obtained by Jeanloz and Thompson [1983]. Filled circle: Yagi et al. [1977]; filled square: Ito and Yamada [1982]; 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

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. Under-binding 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 \(C_{13}, C_{15}\) and \(C_{32}\), respectively.

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 \(\approx 2\%\) [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 \(\left(V_P\right)\) and shear waves \(\left(V_S\right)\), 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]:

\[
M(x) = M_0(1 + b_M x)
\]

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>
<thead>
<tr>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{44})</th>
<th>(C_{55})</th>
<th>(C_{22})</th>
<th>(C_{13})</th>
<th>(C_{15})</th>
<th>(C_{32})</th>
<th>(K)</th>
<th>(G)</th>
<th>(V_P)</th>
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<td>146</td>
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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 \(x = 0\):
  * Wentzcovitch et al. [1998].
  * Karki et al. [1997].
  * Oganov et al. [2001b].
  * Brillouin scattering data from Yeganeh-Haeri [1994].
  * 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 \(V_0 = 159.6 \text{ Å}^3, K_0 = 264.3 \text{ GPa}, K' = 3.94\) and \(V_0 = 160.5 \text{ Å}^3, K_0 = 270.0 \text{ GPa}, K' = 3.96\) for \(x = 0\) and \(x = 0.25\), respectively.
The dependence of the shear modulus on iron content is similar to the dependence of the bulk modulus on iron content. The ratios of obtained from the GGA calculations are similar. These values are much smaller as compared to the ratio in excess of 3, as observed in seismological tomography for the deep lower mantle [Masters et al., 2000]. This indicates that lateral variations of Fe content in (Mg,Fe)SiO₃-perovskite alone can neither account for the observed high values of R nor for an anti-correlation of Vₛ and Vₚ.

We find that R and ξ increase slightly with pressure and we obtain (LDA) 1.46 and 1.62 for R and 0.41 and 0.39 for ξ 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 seismological tomography for the deep lower mantle [Masters et al., 2000]. This indicates that lateral variations of Fe content in (Mg,Fe)SiO₃-perovskite alone can neither account for the observed high values of R nor for an anti-correlation of Vₛ and Vₚ.

References


Kresse, G., and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comp. Mat. Sci., 6, 15–50, 1996b.


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B. Kiefer and L. Stixrude, Department of Geological Sciences, University of Michigan, 425 E. University Ave., Ann Arbor, MI, 48109-1063, USA. (bkiefer@umich.edu; stixrude@umich.edu)

R. M. Wentzcovitch, Department of Chemical Engineering and Materials Science, University of Minnesota, 421 E. University Ave., SE, Minneapolis, MN, 55455, USA; Scuola Internazional Superiore di Studi Avanzati (SISSA), Trieste, Italy. (wentzcov@cems.umn.edu)