Shear waves in the diamond-anvil cell reveal pressure-induced instability in (Mg,Fe)O

Steven D. Jacobsen*,1, Hartmut Spetzler1,*, Hans J. Reichmann3,*, and Joseph R. Smyth§

*Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany; †Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0216; 1Department of Geological Sciences, University of Colorado, Boulder, CO 80309-0399; and 3GeoforschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany

Communicated by Russell J. Hemley, Carnegie Institution of Washington, Washington, DC, March 5, 2004 (received for review February 15, 2004)

The emerging picture of Earth’s deep interior from seismic tomography indicates more complexity than previously thought. The presence of lateral anisotropy and heterogeneity in Earth’s mantle highlights the need for fully anisotropic elasticity data from mineral physics. A breakthrough in high-frequency (gigahertz) ultrasound has resulted in transmission of pure-mode elastic shear waves into a high-pressure diamond-anvil cell using a P-to-S elastic-wave conversion. The full elastic tensor (cij) of high-pressure minerals or metals can be measured at extreme conditions without optical constraints. Here we report the effects of pressure and composition on shear-wave velocities in the major lower-mantle oxide, magnesiowüstite-(Mg,Fe)O. Magnesiowüstite containing more than ~50% iron exhibits pressure-induced c44 shear-mode softening, indicating an instability in the rocksalt structure. The oxide closer to expected lower-mantle compositions (~20% iron) shows increasing shear velocities more similar to MGO, indicating that it also should have a wide pressure-stability field. A complete sign reversal in the c44 pressure derivative points to a change in the topology of the (Mg,Fe)O phase diagram at ~50–60% iron. The relative stability of Mg-rich (MgOFe2O) and the strong compositional dependence of shear-wave velocities (and c66/c44) in (Mg,Fe)O implies that seismic heterogeneity in Earth’s lower mantle may result from compositional variations rather than phase changes in (Mg,Fe)O.

A dense oxide of iron and magnesium is expected to coexist with magnesium silicate perovskite-(Mg,Fe)SiO3 in Earth’s lower mantle at 660- to 2,900-km depth (1). The physical properties of (Mg,Fe)O have been studied extensively by using both static (2–5) and dynamic methods (5–9), but there remains considerable uncertainty surrounding the structure and behavior of (Mg,Fe)O in the lower mantle. Periclase (MgO) has the rocksalt structure to at least 227 GPa (10). On the other hand, wüstitte (FeO) undergoes a displacive phase transition to a rhombohedral distorted B1 structure at ~17 GPa and subsequently to the B8 or NiAs-type structure above 100 GPa (11). Differences in the high-pressure behavior of MGO and FeO imply a change in topology of the (Mg,Fe)O phase diagram, requiring there to be a two-phase field or exsolution gap, but where in composition between ferropericlase (Mg-rich) and magnesiowüstite (Fe-rich) this should occur is not clear yet. Iron-rich compositions (Mg0.1Fe0.9)O and (Mg0.25Fe0.75)O display the rhombohedral distortion above 20 and 60 GPa, respectively (12, 13). At 80–90 GPa and 1,000 K, (Mg0.5Fe0.5)O and (Mg0.6Fe0.4)O were reported to separate into ferropericlase plus FeO in the externally heated diamond-anvil cell (DAC) (14). But in a similar study using a laser-heated DAC, both (Mg0.35Fe0.65)O and (Mg0.25Fe0.75)O were stable in the B1 structure at 100 GPa and 2,500 K (13). A high-spin to low-spin transition in Fe was reported for (Mg0.2Fe0.8)O between ~50 and 60 GPa (15) but without evidence for a volume change or phase stability. Thus, despite concerted efforts to elucidate the structure and stability of (Mg,Fe)O at lower mantle conditions, experiments thus far have led to conflicting results. The search for wave-speed discontinuities in Earth’s lower mantle related to compositional variation or phase changes in (Mg,Fe)O are ongoing (16).

Megahertz-frequency ultrasonics measurements in the multianvil press are a leading resource for experimental thermoelastic data on polycrystalline samples at simultaneous high pressures and temperatures relevant to Earth’s mantle (17). However, single-crystal experiments giving elastic anisotropy (cij) in the multianvil press are relatively few (18). Also at megahertz frequencies, ultrasonic interferometry has been applied successfully to single-crystal samples in the gas- or liquid-pressurized piston-cylinder apparatus (19) and the Paris–Edinburgh cell (20), but these frequencies still limit the minimum sample size to ~1 mm. For microcrystals less than ~0.5 mm in size, as most available synthetic high-pressure mantle phases are, the DAC is the preferred pressure cell, capable of hydrostatic pressures to ~10 GPa with liquid pressure media, and to much higher pressures when loaded with a gas such as helium or neon. Brillouin scattering in the DAC is a powerful method for measuring single-crystal elasticity to pressures now in excess of 50 GPa (21) and temperatures to 1,500 K (22), but as an optical method it is limited to fairly transparent single crystals. Another novel method, impulse-stimulated scattering (23), has been extended recently to include acoustic surface-wave measurements (24) from which shear velocities in opaque minerals or metals are obtained but without P-wave velocities needed for the complete elastic tensor.

By extending the ultrasound to gigahertz frequencies, we reduce acoustic wavelengths in minerals to ~1–10 μm. Pure-mode ultrasonic shear waves have been transmitted into a high-pressure DAC. To resolve some of the questions surrounding (Mg,Fe)O stability, we measured the pressure dependence of S-wave travel times in (Mg,Fe)O crystals ultrasonically to examine the behavior of the c44 elastic constant (=P/2(301)) as a function of composition. This pure-shear mode is the elastic parameter most sensitive to the rhombohedral distortion observed in FeO before the B1–B8 phase transition (11) and therefore should be a useful predictor of (Mg,Fe)O stability. Shear-mode softening (i.e., decreasing shear velocities with increasing pressure) in FeO (25) is the result of strong magnetoelastic coupling driving the B1 (paramagnetic) to rhombohedral (antiferromagnetic) phase transition (26). Mode softening in FeO has also been deduced from lattice strain in nonhydrostatic x-ray diffraction experiments (27), but uncertainties in the magnitude of c44 from such methods are on the order of 15–20%. Our direct (ultrasonic) observations of shear elasticity in (Mg,Fe)O were carried out by using an acoustic shear-wave interferometer for the DAC. The methodological advance not only has broad application to high-pressure research in Earth
and materials sciences but also for development of an absolute pressure scale (21, 28).

Experimental Methods

The acoustic interferometer is based on our first-generation gigahertz-ultrasonic delay line (29). In its initial form, gigahertz-ultrasonic interferometry was well suited for high-pressure experiments in the DAC (30, 31) but limited to P-wave experiments by the absence of commercially available shear-wave transducers operating at gigahertz frequencies. Here we describe an acoustic P-to-S conversion buffer rod for high-pressure shear elasticity experiments in the DAC, pictured in Fig. 1. The buffer rod works on the principle of Snell’s Law. A P-wave traveling in the [100] direction of an yttrium aluminum garnet crystal buffer rod (Fig. 1A) is incident on a conversion facet, cut at a specific angle to produce a converted S-wave at 90° to the incident P (Fig. 1B). For cubic materials, the angle of incidence producing an orthogonal conversion from Snell’s Law is given by tan(θ) = VP/VS. For optical yttrium aluminum garnet, we determined i = 59.5° from bench-top measurements of VP and VS. The initial compression waves are produced by a ZnO thin-film P-transducer, sputtered directly onto the side of the buffer rod. The P-transducer (and conversion to shear) is operable over a very broad bandwidth, typically from ∼0.5 to >2.0 GHz. By forcing the conversion to occur at 90°, the direction of particle motion is preserved across the conversion. Both P- and S-waves propagate in pure-mode directions [100] of the single-crystal buffer rod, and therefore the polarization is precisely known. Shear waves produced in this way are of much higher quality than those usually generated (at megahertz frequencies) by shear-wave transducers, because there is no P-wave contamination. We suggest that shear-wave generation by this method might be a useful replacement for traditional shear-wave transducers altogether in other ultrasonic applications.

The interferometer uses a continuously running, highly stable frequency synthesizer that provides phase coherence throughout a measurement. This is akin to the use of a laser in an optical interferometer and allows us to measure ultrasonic travel times to a small part of an interference fringe or ∼1 part in 108 if the round-trip travel-time through a sample is ∼100 ns (sample thickness of 300–500 μm) and to 1 part in 102 if it is an order of magnitude shorter (sample thickness of 30–50 μm). The continuous signal is gated with a pulse generator, allowing the introduction of short tone bursts. Impedance contrasts at the buffer-rod–diamond interface, diamond–sample interface, and sample–pressure medium interface produce reflections, which return and reconvert to P, and are finally detected by the source transducer. The entire round trip through the system is typically ∼3 μs. The time difference between the diamond and the first sample echo is usually very short (8–20 ns) compared with the width of the input signal (∼100 ns). An interference pattern is produced by measuring the amplitude of the combined signal at a position where there is first-order interference (between the diamond and sample echoes) and scanning the frequency (Fig. 2). Shear-wave travel times are determined from each fitted frequency maxima and minima of interference (29).

The samples are prepared as oriented single-crystal plates: polished with parallel faces and flat to ∼1/10a with thicknesses ranging from ∼20 to 40 μm. The plates have a finishing polish of optical quality and are placed directly on the culet of the acoustic transmitting anvil. A small force is applied to the sample by adding silica aerogel to a liquid 16:3:1 methanol/ethanol/water pressure-transmitting medium. The aerogel has a very high porosity (>90%) and acts as a spring to gently press the sample against the anvil. In this way, we avoid the use of messy glues or foils to achieve acoustic coupling between the sample and the diamond. We presume that a very thin layer of the fluid pressure medium is present under the sample to an extent determined by the equilibrium between the relative magnitudes of the normal force transmitted from the aerogel and the surface tension of the fluid. Pressures >10 GPa were routinely reached, but the aerogel-alcohol mixture is hydrostatic to only ∼9 GPa, where the glass transition was observed by the onset of shear-wave transmission completely through the sample chamber (i.e., a diamond culet-to-culet reflection was detected around this pressure but always before the sample bridged the anvils). Pressures were determined by using the ruby fluorescence scale (32).

Shear-wave travel times were measured as a function of pressure in [100]-oriented single-crystal (Mg,Fe)O. The samples were synthesized by the interdiffusion of Fe and Mg between single-crystal MgO and prereacted magnesiowüstite powders (5). Sample nomenclature is Fe(1 fulfillment)/Mg, where X gives the atomic ratio Fe/(Fe + Mg). The crystal of pure iron-wüstite has the non-stoichiometric formula Fe0.95O.

Results and Discussion

Measured shear-wave travel times for (Mg,Fe)O are plotted in Fig. 3A. The velocities shown in Fig. 3B are calculated from the travel times by using the sample thicknesses. The initial sample thicknesses were determined in each case by measuring the zero-pressure travel time and converting to thickness by using the bench-top velocities (5). The change in length with pressure was calculated from their equations of state over the same pressure range (5). Shear velocities along [100] decrease with increasing...
pressure for wüstit FeO and magnesiowüstite samples Fe78 and Fe56, with \( \frac{\partial v_3^{(100)}}{\partial P} = -42(\pm 1), -26.9(\pm 0.4), \) and \(-15.2(\pm 0.2)\) m s\(^{-1}\) GPa\(^{-1}\). However, for ferropericlase containing \( \approx 24\% \) iron, the sign of \( \frac{\partial v_3^{(100)}}{\partial P} \) switches and is \( 11(\pm 1)\) m s\(^{-1}\) GPa\(^{-1}\). The results demonstrate that increasing Mg content in (Mg,Fe)O acts to stabilize the B1 structure at high pressures.

The \( c_{44} \) elastic constants were calculated from the shear velocities as a function of pressure. The results are plotted in Fig. 4, with polynomial fits given in Table 1. For the cubic structure, this term of the elastic tensor provides an important proxy for the cubic body diagonal stiffness (11). The second-order displacive phase transition observed at room temperature for FeO at \( \approx 17 \) GPa (11), for \((Mg_{0.1}Fe_{0.9})O\) at \( \approx 20\) GPa (12), and for \((Mg_{0.25}Fe_{0.75})O\) at \( \approx 60\) GPa (13) is a rhombohedral distortion of the B1 structure. The distortion occurs by elongation of the body diagonal (111) and therefore should be revealed by mode softening in \( c_{44} \). Polynomial fits to \( c_{44} \) with pressure indicate significant reduction in this elastic constant for FeO and Fe78 on the order of \( 20\% \) and \( 13\% \), respectively, over this pressure range. Although we still observe decreasing \( c_{44} \) with pressure in Fe56, it is \(< 2\% \) at 10 GPa, thus the change in topology of the (Mg,Fe)O high-pressure phase diagram is expected to occur at iron contents higher than \( \approx 60\% \) FeO or \((Mg_{0.6}Fe_{0.4})O\), consistent with recent in situ high \( P-T \) diffraction studies (13).

The spin state of iron in (Mg,Fe)O at lower-mantle conditions has major implications for the density, composition, and seismic structure of Earth’s lower mantle. A transition from the usual high-spin state of iron to the low-spin state in (Mg,Fe)O was reported at pressures above \( \approx 50\) GPa by using x-ray emission spectroscopy (15). The authors postulate that the spin-state transition influences Fe-Mg partitioning between magnesiowüstite and (Mg,Fe)S\(_2\)-perovskite enough to nearly deplete the perovskite of iron at depths below the transition. Although the authors were unable to report associated volume changes in the \((Mg_{0.6}Fe_{0.4})O\) in situ, the spin-state transition is expected to decrease effective ionic radius of Fe by as much as \( 10\% \). Therefore, even with only \( 10-20\% \) Fe in (Mg,Fe)O, a rather large \( (\approx 2-5\% \) volume change is expected to occur. The decrease in mean M-O bond distances (and shortened O...O interatomic distances) in the rocksalt structure containing low-spin iron therefore should exhibit increased compressional and shear-wave velocities as the strong O...O repulsive forces become highly incompressible. In this study, we have shown that there is a strong dependence of shear velocities on the iron content in (Mg,Fe)O, especially at higher pressures. Given that a change in the spin state of iron should also influence the Mg-Fe partitioning in the mantle, it is not clear yet how a high-spin to low-spin transition in iron will affect seismic wave velocities in the lower mantle, but any increase in the shear elastic moduli brought on by the volume change might be dampened by reduced shear velocities associated with an increasing Fe/Mg ratio in (Mg,Fe)O.

The advent of acoustic shear waves in the DAC has made possible direct observation of shear-mode softening in major lower-mantle phase (magnesiowüstite) and tripled the pressure range over which similar behavior has been measured in FeO.

Table 1. Variation of the \( c_{44} \) elastic constant of (Mg,Fe)O with pressure

<table>
<thead>
<tr>
<th>Composition</th>
<th>( c_{44} ), GPa</th>
<th>( P_{\text{max}} ), GPa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>45.5(1) – 1.03(2)P – 0.014(3)P(^2)</td>
<td>3 (ultrasonic)</td>
<td>25</td>
</tr>
<tr>
<td>FeO</td>
<td>46.09(7) – 0.86(4)P – 0.024(4)P(^2)</td>
<td>8.4 (ultrasonic)</td>
<td>This study</td>
</tr>
<tr>
<td>Fe78</td>
<td>63.42(6) – 0.91(3)P – 0.004(3)P(^2)</td>
<td>9.1 (ultrasonic)</td>
<td>This study</td>
</tr>
<tr>
<td>Fe56</td>
<td>83.44(4) – 0.14(2)P – 0.003(2)P(^2)</td>
<td>8.8 (ultrasonic)</td>
<td>This study</td>
</tr>
<tr>
<td>Fe24</td>
<td>123.3(2) + 1.24(5)P</td>
<td>7.2 (ultrasonic)</td>
<td>This study</td>
</tr>
<tr>
<td>MgO</td>
<td>155.7(5) + 1.09(7)P – 0.0047(16)P(^2)</td>
<td>55 (Brillouin)</td>
<td>21</td>
</tr>
<tr>
<td>MgO</td>
<td>158.8(2) + 1.11(1)P – 0.016(3)P(^2)</td>
<td>3 (ultrasonic)</td>
<td>19</td>
</tr>
<tr>
<td>MgO</td>
<td>154.4(20) + 0.84(20)P + 0.003(10)P(^2)</td>
<td>18.6 (Brillouin)</td>
<td>37</td>
</tr>
</tbody>
</table>
Here we observe an increase in the derivative with theoretical predictions for stoichiometric (Mg,Fe)O (6). The FeO is wüstite (FeO$_{33}$), and otherwise the labels (FeX) indicate the atomic ratio X = Fe/(Fe + Mg). (B) Fe-rich (Mg,Fe)O exhibits decreasing shear velocities with increasing pressure. Previous ultrasonic results for FeO (25) are plotted with a solid curve.

Although we detect a structural instability in Fe-rich magnesiowüstite, the elastic derivative $\partial c_{sl}/\partial P$ switches (becoming positive) for ferropericlase (Fe24) and is more similar to MgO than magnesiowüstite Fe56 (Fig. 4 and Table 1). Because of the nature of the high-pressure rhombohedral distortion in magnesiowüstite (body-diagonal elongation), the results provide direct evidence for a systematic increase in the high-pressure stability of the B1 structure for (Mg,Fe)O with increasing Mg content.

Previous static compression experiments (5) indicate that there is a small initial increase in the bulk modulus (and $\partial K/\partial P$) for (Mg,Fe)O with iron contents up to $\sim$25% FeO, consistent with theoretical predictions for stoichiometric (Mg,Fe)O (6). Here we observe an increase in the derivative $\partial c_{sl}/\partial P$ by almost 13% between MgO and (Mg,Fe)O containing $\sim$25% FeO. A complete switching in the high-pressure elastic behavior of (Mg,Fe)O points to a change in the topology of the (Mg,Fe)O phase diagram at $\sim$50–60% iron, consistent with previous in situ x-ray diffraction studies (13). The observed shear-mode softening in Fe-rich (Mg,Fe)O is likely due to strong magnetoelastic coupling [as in FeO (26)] driving potential magnetic and structural phase transitions. The results indicate that B1-structured ferropericlase is expected to have a similar pressure-stability field as MgO, which is stable at pressures throughout Earth’s lower mantle (10).

We thank Hubert Schulze, Klaus Müller, Georg Hermannsdorfer, Heinrich Ohlmeier, Sven Lindenhardt, Kurt Klasinski, Jeffrey Cooper, and Stephen Mackwell for their assistance. We also thank Jung-Fu Lin, Russell Hemley, Ho-kwang Mao, and Ian Jackson for useful discussions and critique of the manuscript. This work was supported by the Deutsche Forschungsgemeinschaft, the National Science Foundation, and the Alexander von Humboldt Foundation.

Fig. 3. Pressure-induced shear instability is detected in Fe-rich (Mg,Fe)O. (A) The observed ultrasonic travel times (filled circles) are plotted against pressure. The FeO is wüstite (FeO$_{33}$), and otherwise the labels (FeX) indicate the atomic ratio X = Fe/(Fe + Mg). (B) Fe-rich (Mg,Fe)O exhibits decreasing shear velocities with increasing pressure. Previous ultrasonic results for FeO (25) are plotted with a solid curve.

Fig. 4. A complete sign reversal in the pressure derivative of the shear elasticity ($\partial c_{sl}/\partial P$) in (Mg,Fe)O indicates a pressure-induced structural instability for Fe-rich compositions. Elastic constant data from this study are shown by filled circles with dashed-line fits (given in Table 1). Also plotted are previous ultrasonic data to 3 GPa (solid curves) for MgO (19) and FeO (25) as well as data for MgO from Brillouin scattering [dash-dot (21) and dotted (37) curves]. Shear-mode softening in (Mg,Fe)O may be due to strong magnetoelastic coupling [as in FeO (26)], driving potential magnetic and structural phase transitions. The results indicate that B1-structured ferropericlase is expected to have a similar pressure-stability field as MgO, which is stable at pressures throughout Earth’s lower mantle (10).


