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Gigahertz ultrasonic interferometry at high P and T : new tools for obtaining a thermodynamic equation of state

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Abstract

A new method of generating shear waves with near-optical wavelength has been developed for gigahertz ultrasonic interferometry. The new acoustic technique features a P-to-S conversion upon reflection inside an MgO buffer rod, and is used first to determine the full set of ambient P - T elastic constants (c_{ij}) of magnesiowüstite—(Mg, Fe)O. In addition, P-wave travel times have been measured in olivine to 250 °C at ~ 2.5 GPa in a resistance-heated ultrasonic diamond anvil cell, demonstrating that acoustic coupling can be maintained at high temperature in a hydrostatic (alcohol) pressure medium. The new methodology brings us closer to obtaining a complete travel-time equation of state for single-crystal samples.

1. Introduction

Knowledge of the elastic properties and crystal chemistry of minerals plays an important role in interpreting the composition and mineralogy of the Earth's interior from seismological observation. Gigahertz ultrasonic interferometry (GUI) is a relatively new tool among the arsenal of acoustic and optical methods that are used to measure elastic-wave travel times or velocities in solids for determination of elastic moduli [1].

In recent years, GUI has successfully reduced the sample-size requirements for single-crystal ultrasonics to about 50 μm , causing manifold increase in the variety of natural and synthetic phases that can be studied with this method. In turn, small sample sizes motivated interfacing the GHz technology with a diamond anvil cell (DAC) [2], where P-wave measurements have been carried out on MgO to a maximum hydrostatic pressure of 6 GPa [3] and to 207 °C at 4.5 GPa in a solid KBr pressure medium [4]. However, GUI

has been essentially without shear waves. Earlier attempts to thin down a modified LiNbO₃ piezoelectric shear transducer (to $\sim 30 \mu\text{m}$) produced only relatively low-quality shear over the narrow frequency band from about 590–605 MHz [5]. Shear is required for determination of the complete set of elastic constants (c_{ij}) and isotropic bulk (K_S) and shear (G) moduli of minerals.

Here we present a new method of generating shear waves with near-optical wavelength. The new acoustic technique features a P-to-S conversion upon reflection inside a single-crystal MgO buffer rod, and is used first to determine the complete set of elastic constants for (Mg, Fe)O with compositions spanning the solid solutions [6, 7]. (Mg, Fe)O is a dense monoxide of the nominally B1 or rock-salt structure that is expected to coexist with silicate perovskite—(Mg, Fe, Al)(Si, Al)O₃—in the Earth's lower mantle (660–2900 km depth). In the DAC, [100] P-wave measurements have been made on (Mg_{0.423}Fe_{0.541}Al_{0.036})O to 3.6 GPa, resulting in determination of $\partial c_{11}/\partial P$. Also, P-wave travel times have been measured in San Carlos olivine to 2.5 GPa and 250 °C without a bonding agent between the sample and the anvil. We are exploring the use of aerogel as a transparent 'spring' for pressing an ultrasonic sample against the acoustic transmitting anvil at high temperature.

If both P- and S-wave travel times can be measured at high pressures and temperatures, the complete travel time equation of state (CT-EoS) described by Spetzler *et al* [8, 9] may be obtained. If the CT-EoS is measured in conjunction with an independent equation of state (e.g. with x-rays), the variable pressure is determined by two independent volume (density) measurements, resulting in an absolute pressure scale.

2. Experimental details

Seismologists have long known about the conversion of elastic-wave particle motion in solids between compressional (P) and shear (S) upon reflection. We borrowed this idea to generate GHz-frequency shear waves by P-to-S conversion on the internal facet of an oriented MgO prism. The input P wave is generated at a sputtered ZnO thin-film transducer. The incident P wave strikes the conversion facet of the prism at an angle of incidence such that the incident P wave is orthogonal to the reflected S wave. This geometry takes advantage of the orthogonal pure-mode [100] directions in cubic MgO, as well as forcing the symmetric return of the elastic wave (PSSP) for detection at the source transducer. For MgO, the angle of incidence (θ_{ip}) is 54°. Another important advantage of using P-to-S conversion in a prism is that the shear polarization direction is precisely known. The new bench-top shear-wave generator is illustrated in figure 1.

Interferometry is performed by bonding a sample to the prism face which back-reflects the S wave. A set of two tone bursts are introduced into the prism, spaced in time such that the second PSSP echo overlaps with the first sample echo. The frequency is stepped, and an interference pattern is produced (figure 1), from which the travel time as a function of frequency is determined. In this way, we have produced purely transverse wave energy observed continuously from 0.6 to 2.1 GHz.

The shear-wave prism was first used to measure the elastic constants of (Mg, Fe)O. Two suites of (Mg, Fe)O single crystals were prepared with varying degrees of non-stoichiometry by interdiffusion of Fe and Mg between single-crystal periclase (MgO) and pre-reacted (Mg, Fe)O powders. Interdiffusion was carried out in a gas furnace operating at 1450 °C and 10^{-2} Pa oxygen fugacity (f_{O_2}) for approximately 200 h. The furnace was cooled at a rate of about 300 °C h⁻¹. Microprobe analysis reveals that the Fe distribution in the single crystals is homogeneous at the level of sampling, about every 10–20 μm . The first suite of (Mg, Fe)O single crystals have $\sum \text{Fe}/(\sum \text{Fe} + \text{Mg})$ ratios of 0.058, 0.149, 0.270, 0.366, 0.561, and 0.749. A second suite of samples having $\sum \text{Fe}/(\sum \text{Fe} + \text{Mg})$ ratios of 0.239, 0.527, and 0.783 were

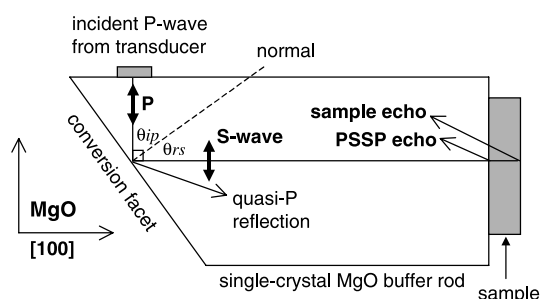


Figure 1. The P-to-S shear-wave prism.

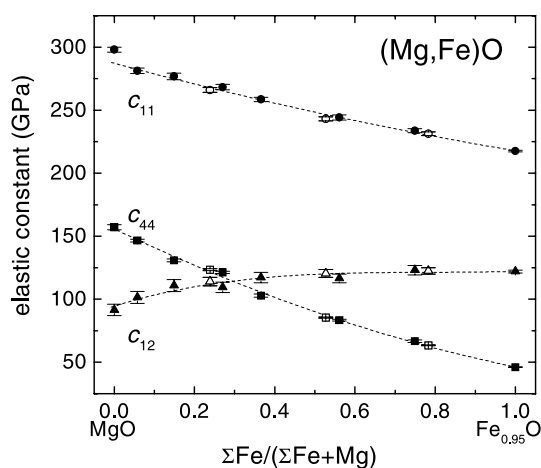


Figure 2. Variation of the elastic constants with composition for (Mg, Fe)O. The more stoichiometric suite is represented by open symbols.

prepared in the same way. However, these samples were subsequently annealed at 1300°C and 10^{-5} Pa f_{O_2} for 20 h and quenched at about $30^{\circ}\text{C s}^{-1}$. Ferric iron contents (found by Mössbauer spectroscopy) range from 1 to 13% of the total Fe, but the re-annealed suite is more stoichiometric [7].

Compressional and shear-wave travel times were measured in the [100] and [111] directions for all the (Mg, Fe)O samples. The thickness of the samples ranges from about 200 to $700\ \mu\text{m}$, measured using a digital micrometer with an accuracy of $\pm 1\ \mu\text{m}$. The orientation of the samples was checked to be within $\pm 1^{\circ}$ by the x-ray precession method. Combined with sample densities calculated from the measured cell parameters and compositions, the velocities were used to calculate the variation of the elastic constants with composition $x = \sum \text{Fe} / (\sum \text{Fe} + \text{Mg})$, also plotted in figure 2:

$$c_{11} = 287(2) - 85(9)x + 16(7)x^2 \text{ GPa} \quad (1)$$

$$c_{12} = 95(3) + 99(23)x - 123(51)x^2 + 51(31)x^3 \text{ GPa} \quad (2)$$

$$c_{44} = 156(2) - 154(7)x + 44(5)x^2 \text{ GPa}. \quad (3)$$

The rate of change in the elastic constants with composition is greatest between MgO and (Mg, Fe)O with ~ 25 mol% FeO, such that adding Fe into periclase has a greater effect on the elastic properties than adding Mg to wüstite. The elastic properties of (Mg, Fe)O having similar total Fe, but varying Fe^{3+} contents are identical within uncertainty.

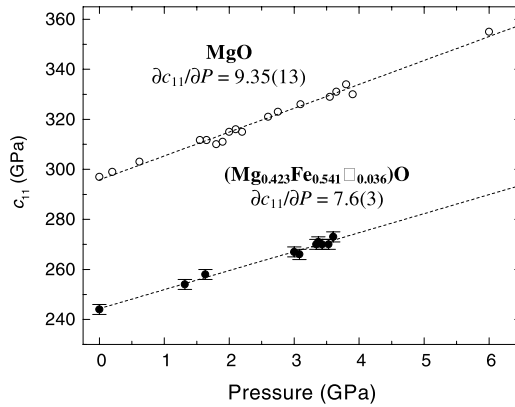


Figure 3. Variation of the elastic constant c_{11} with pressure for MgO [10] and (Mg, Fe)O containing ~ 56 mol% FeO.

A sample of (Mg, Fe)O with $\sum \text{Fe}/(\sum \text{Fe} + \text{Mg}) = 0.56$ (13% ferric) was selected for high-pressure ultrasonics. This sample was chosen in part because it is also the subject of a single-crystal static compression study to 9 GPa, so the measured K_{0T} and K' [7] may be used in calculations of the change in length with pressure. The zero-pressure parameters are: $\rho_0 = 4847(19) \text{ kg m}^{-3}$; $a_0 = 4.2621(2) \text{ \AA}$; $K_{0T} = 156(1) \text{ GPa}$; $V_P^{[100]} = 7096(25) \text{ m s}^{-1}$, resulting in $c_{11} = 244(2) \text{ GPa}$.

The cell was loaded with a 4:1 methanol:ethanol pressure medium along with several rubies to determine the pressure. The [100] P-wave travel time was measured at nine different pressures up to 3.6 GPa. At each pressure, the sample length and density were obtained from the P - V equation of state. The travel times, sample length, and density were used to calculate the [100] P-wave velocity and elastic constant c_{11} as a function of pressure. For this composition, we obtain $\partial V_P^{[100]}/\partial P = 85(5) \text{ (km s}^{-1} \text{ GPa}^{-1})$ and $\partial c_{11}/\partial P = 7.6(3)$. The variation of c_{11} with pressure for the iron-bearing phase is shown in figure 3 against MgO with $\partial c_{11}/\partial P = 9.35(13)$ obtained in a similar experiment by Reichmann *et al* [3].

In a similar DAC, a sample of [001]-oriented San Carlos olivine ($\text{Fe}_{0.90}$) was loaded in a 4:1 methanol:ethanol pressure medium with ruby. In this unusual case, a very good ultrasonic signal was obtained from the sample without any bonding agent, such as glue. The open-cell travel time of 22.72(2) ns was obtained, giving an initial length of 94.8 μm , calculated from the zero-pressure elastic constant $c_{33} = 233.5 \text{ GPa}$ reported by Abramson *et al* [10] for San Carlos olivine. The pressure was raised, and [001] P-wave travel times were measured to a maximum pressure of 2.5 GPa, resulting in $\partial c_{33}/\partial P = 5.6(2)$. The high- P San Carlos data are shown in figure 4(a).

At the highest pressure ($\sim 2.5 \text{ GPa}$), the temperature was raised and P-wave travel times were measured at 100, 180, and 250 $^{\circ}\text{C}$, shown in figure 4(b). High temperatures are achieved with an external resistance heater of Mo wire wrapped around the carbide seats. The upper and lower anvils are heated independently by two temperature controllers reading the thermocouple in contact with each diamond. The cross-pressure cross-temperature derivative of c_{33} is not calculated here because the pressure could not be measured at simultaneously high temperatures. However, this pilot experiment illustrates that acoustic coupling can be maintained at high temperatures ($\leq 250 \text{ }^{\circ}\text{C}$) in a liquid pressure medium, motivating future single-crystal ultrasonic measurements at simultaneously high P and T .

A major problem facing future single-crystal ultrasonic measurements at high temperature will be keeping the sample against the acoustic transmitting anvil. We are exploring the use

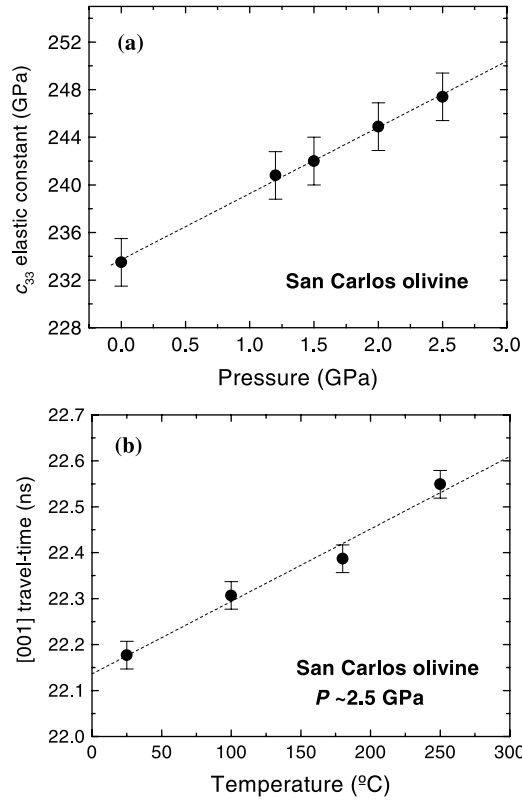


Figure 4. (a) Variation of c_{33} with pressure in [001] San Carlos olivine. (b) Variation of the P-wave travel time with temperature at ~ 2.5 GPa.

of aerogel as a transparent spring to be loaded with the sample. Recently, we produced wet silica alcogel in a 4:1 methanol:ethanol fluid. A crystal of quartz was loaded in a DAC packed tightly with the alcogel and has so far exhibited hydrostatic compression to 5 GPa based on the axial ratio c/a .

3. Application to equations of state

Here we report on two important developments in GUI. One, shear waves with near-optical wavelength have been made with existing P-wave transducers by P-to-S conversion. Two, acoustic coupling (with P waves) has been maintained between a sample and a diamond anvil at high temperatures (up to 250 $^{\circ}\text{C}$) without a bonding agent in a hydrostatic (alcohol) pressure medium. Possibly, the most powerful application of obtaining high-precision P- and S-wave travel times at high P and T will be determination of the CT-EoS.

The CT-EoS is formulated in detail by Spetzler and Yoneda [8]. Briefly, P and S travel times are to be obtained as a function of pressure and temperature: $t_P(P, T)$ and $t_S(P, T)$. In addition, knowledge of ρ_0 and l_0 (the initial density and sample length), along with the thermal expansivity (α) and the heat capacity (C_P) as a functions of temperature at zero pressure are required. First, t_P and t_S at $P = 0$ are used to calculate V_P and V_S as a function of temperature using l_0 and the change in length determined by $\alpha(T)$. The velocities can then be used to

calculate the zero-pressure adiabatic moduli $K_{0S}(T)$ and $G_0(T)$ using $\rho(T)$, calculated from $\alpha(T)$. Since the heat capacity is known as a function of temperature, the Grüneisen relation can be used to convert the adiabatic bulk modulus to the isothermal one $K_{0T}(T)$ which, in turn, can be used to calculate the density and sample length for a small pressure step. At the first pressure, the same process is used to obtain the parameters as a function of temperature. This requires knowledge of $\partial C_P/\partial P$ and $\partial\alpha/\partial P$ at constant temperature, which can be determined using the parameters already known [8]. In this way, the CT-EoS delivers the thermodynamic variables: ρ , α , C_P , V_P , V_S , K_S , K_T , and G at any P and T within a reasonable range of the experiment. If an independent EoS can be measured simultaneously (e.g. with x-rays), the two density measurements can be set equal and the absolute pressure is determined. This idea was recently explored with MgO using the alternative combination of Brillouin scattering and x-ray diffraction to 55 GPa (at ambient temperature) by Zha *et al* [11].

We are working towards focusing the new tools of GUI towards obtaining the CT-EoS in the modest, but hydrostatic pressure range to 10 GPa (in alcohol) and at temperatures to 400 °C. This range is attainable in our new miniature three-pin ultrasonic/x-ray diamond cell, and should be large enough to obtain meaningful P - T derivatives [8]. Once both P- and S-wave travel-time measurements can be made at high P and T in the DAC, the full potential of GUI can be realized.

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