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Elasticity and equation of state of orthoenstatite, $MgSiO_3$

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ABSTRACT

Published measurements of the compression and elasticity of $MgSiO_3$ orthoenstatite have been reanalyzed and the estimates that they yield of the room pressure bulk modulus and its pressure derivative are now shown to be consistent with one another. New single-crystal compression data is also consistent with the revised EoS parameters. Combining the results of four different experiments (two compression, one Brillouin measurement, and one in situ high-pressure ultrasonic measurement) yields best estimates of K_{T0} = 105.8(5) GPa and K'_0 = 8.5(3) for a third-order Birch-Murnaghan EoS.

INTRODUCTION

Magnesium silicate of pyroxene stoichiometry, $MgSiO_3$, is a major component of the Earth's mantle. The phase equilibria of the pure end-member composition and the physical properties of the stable phases are therefore often used as a zero-order model for the behavior of the orthopyroxene component of mantle assemblages. Thus, for example, the inversion from orthoenstatite to high-pressure *C*2/*c* clinoenstatite has been associated with the enigmatic "X" discontinuity located at 300 km depth on the underside of subducting slabs (Woodland 1998). However, the elasticity and equations of state of orthopyroxenes have been the subject of controversy ever since Frisillo and Barsch (1972) suggested that the pressure derivative K'_{T0} of the bulk modulus of a bronzite orthopyroxene, $Mg_{0.8}Fe_{0.2}SiO_3$, had an anomalously high value of 9.42. A subsequent measurement of $MgSiO_3$ orthoenstatite by in situ high-pressure ultrasonic interferometry (Ito et al. 1977) confirmed this result but was not generally accepted. Subsequent experimental efforts concentrated upon measuring the effect of composition on the ambient-pressure elastic properties of orthopyroxenes, whose other major chemical component is ferrosilite, $FeSiO_3$, with lower levels of substitution of Ca, Al, and other cations.

Improvements in high-pressure single-crystal X-ray diffraction techniques in the early 1990s resulted in the volume variation with pressure of orthopyroxenes being measured sufficiently precisely to allow both the room pressure bulk modulus, K_{T0}, and its pressure derivative at room pressure, K'_0, to be determined. A single-crystal study of synthetic $MgSiO_3$ orthoenstatite to a pressure of 8.5 GPa (Angel and Hugh-Jones 1994) yielded EoS parameters of K_{T0} = 103(2) GPa and K'_0 = 9.2(6). However, an associated structural study of the evolution with pressure of the orthoenstatite structure suggested that there is a change in compression mechanism at about 4 GPa. This, together with an apparent deviation in the low pressure *P-V* data that we discuss below, led to the authors fitting the *P-V* data in two parts. This resulted in a room pressure bulk modulus of K_{T0} = 96(3) GPa, significantly less than the value of K_{T0} ~106 GPa obtained from Brillouin measurements (Weidner et al. 1978; Jackson et al. 1999). The extension of ultrasonic interferometric measurements to higher pressures in the multi anvil has yielded parameters K_{T0} = 109(2) GPa and K'_0 = 7.0(4) for a third-order EoS (Flesch et al. 1998). However, a significant fourth-order component to the elasticity was suggested by curvature in data at the highest pressures achieved. These differences in EoS parameters are important because they result in significant differences in the predicted density of orthoenstatite at upper-mantle pressures (Fig. 1).

In view of these significant discrepancies we have undertaken a reanalysis of all previously published data on the compression and elasticity of end-member orthoenstatite. We have also remeasured the compression curve of two crystals of the same material that was recently measured by Brillouin spectroscopy (Jackson et al. 1999).

EXPERIMENTAL DETAILS

Compression data were obtained from two single crystals of the orthoenstatite sample originally synthesized by Ito (1975), kindly supplied by G. Rossman. The two crystals were a portion of the sample used in the recent Brillouin measurement (Jackson et al. 1999). Each crystal was measured in a BGI-type diamond-anvil cell (Allan et al. 1996) using a 4:1 mixture by volume of methanol and ethanol to provide a hydrostatic pressure medium. High-pressure unit-cell data were collected on the Huber diffractometer of the Bayerisches Geoinstitut with the techniques described by Angel et al. (2001). Pressures were determined from the EoS of a quartz crystal (Angel et al. 1997) included in the cell. EoS parameters were obtained from both

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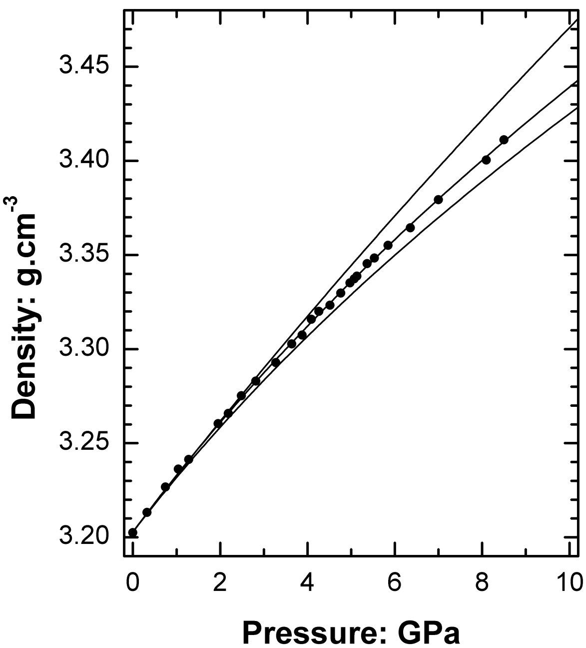

FIGURE 1. The variation with pressure of the density of $MgSiO_3$ orthopyroxene. Points are the *P-V* data collected by Angel and Hugh-Jones (1994). The lines represent various equations of state, from top: K_{T0} = 106 GPa and K'_0 = 4, K_{T0} = 102.3 GPa and K'_0 = 9.2, K_{T0} = 106 GPa and K'_0 = 10.7.

this new data and the previously reported compression data by fully weighted fits of the Birch-Murnaghan EoS performed with the EosFit software (Angel 2001).

DISCUSSION

Direct measurements of the elasticity of a solid by Brillouin spectroscopy and ultrasonic interferometry yield the adiabatic bulk modulus, K_{so}. Single-crystal compression studies yield the isothermal bulk modulus, K_{T0}. Comparison of the results from these two types of measurement therefore requires the conversion factor $(1 + \alpha_V \gamma T) = K_{so}/K_{T0}$ where α_V is the coefficient of volume expansion and γ is the Gruneisen parameter. The many experimental measurements of α_V of orthopyroxenes were recently reviewed by Hugh-Jones (1997). There seems to be a convergence of recent measurements towards a value of 3.2×10^{-5} K^{-1} at room temperature (Hugh-Jones 1997; Zhao et al. 1995; Jackson et al. 2001), although Yang and Ghose (1994) obtained a significantly lower value of $\alpha_V = 2.35 \times 10^{-5}$ K^{-1}.

Reported values of the Gruneisen parameter for orthoenstatite range from 0.88 (Yang and Ghose 1994) to 1.28 (Chopelas 2000), although it should be noted that many estimates of this parameter are necessarily correlated with the value used or obtained for the thermal expansion coefficient. A survey of the literature indicates that estimates of the conversion factor $(1 + \alpha_v \gamma T)$ range from 1.006 (Yang and Ghose 1994) to 1.012 (Chopelas 2000) at 300 K. We therefore employ a value of 1.009, being an average of these two extreme values, and assign an uncertainty of 0.003 that is incorporated into the uncertainties of K_{T0} derived from adiabatic measurements of K_{S0}.

The relationship between the isothermal pressure derivatives of K_{T0} and K_{S0} is, following Anderson (1995):

$$K'_{S0} = K'_{T0}\,(1 + \alpha_v \gamma T) - \alpha_v \gamma T\,(\delta_T + q)$$

$$\text{in which } q = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T.$$

Because the first term in this equation, $(1 + \alpha_v \gamma T)$, is approximately 1.01 and $K'_{S0} > K'_{T0}$ we estimate that K'_{S0} and K'_{T0} differ by less than 0.1. This difference is significantly less than the uncertainty in any experimental measurement of a pressure derivative of the bulk modulus, so no such correction has been made in the following analysis.

Finite strain, or f_E-F_E, plots in which $F_E = P/3f_E(1 + 2f_E)^{5/2}$ is plotted against $f_E = [(V_0/V)^{2/3} - 1]/2$, are a useful diagnostic tool to examine compression data because they are more sensitive than direct plots of volume against pressure to small changes in EoS parameters. Thus, a Birch-Murnaghan third-order EoS becomes an inclined straight line in an f_E-F_E plot, whereas a fourth-order Birch-Murnaghan EoS becomes a curved line. The value of F_E at $f_E = 0$ is equal to the room pressure bulk modulus K_{T0}. When the data of Angel and Hugh-Jones (1994) are displayed as an f_E-F_E plot, with the experimental room-pressure volume measurement used as V_0, the lower-pressure data deviate from the linear trend defined by the higher-pressure data (Fig. 2a). This deviation and apparent break in slope at a pressure of ~4 GPa led Angel and Hugh-Jones (1994) to describe the data with two separate EoS, and to derive a room-pressure bulk modulus of K_{T0} = 96(3) GPa, which is inconsistent with Brillouin measurements (Weidner et al. 1978; Jackson et al. 1999). However, such deviations or apparent curvature in an f_E-F_E plot can also occur as a result of using an incorrect value of V_0 to calculate the f_E values. Note that an error in V_0 of only 0.05% is sufficient to produce significant curvature in the plot and displacement of K_{T0} by ~15% (see Fig. 3b in Angel 2001).

Furthermore, an incorrect measurement of the room-pressure volume can also significantly bias least-squares fits of *P-V* data to obtain the EoS parameters, even when V_0 is refined in the process. Because the uncertainty in room pressure (~10^{-6} GPa) is far less than the uncertainty in high-pressure measurements (~0.01–0.03 GPa), the room-pressure datum is more heavily weighted (by a factor of 5–6 in this case) than the high-pressure data. This weighting causes the V_0 parameter to be heavily influenced by the observed room-pressure volume measurement which, if incorrect, will also lead to incorrect values for K_{T0} and K'_0 because of parameter correlation in the least-squares refinement. We therefore performed a new refinement of the EoS parameters to the *P-V* data set of Angel and Hugh-Jones (1994). When the observed room-pressure datum is included the EoS parameters are V_0 = 832.89(11) Å^3, K_{T0} = 102.3(1.2) GPa and K'_0 = 9.2(5), and the weighted-chi-squared value, χ^2_w, is 1.5. This EoS is represented by the straight line in Figure 2a. But when the measured room-pressure datum is excluded from the data set the refined value of V_0 becomes 832.5(2) Å^3, approximately 2.5 estimated standard deviations (e.s.d.'s) less than the observed value of the room pressure volume, and χ^2_w drops significantly to 1.3. The refined parameters

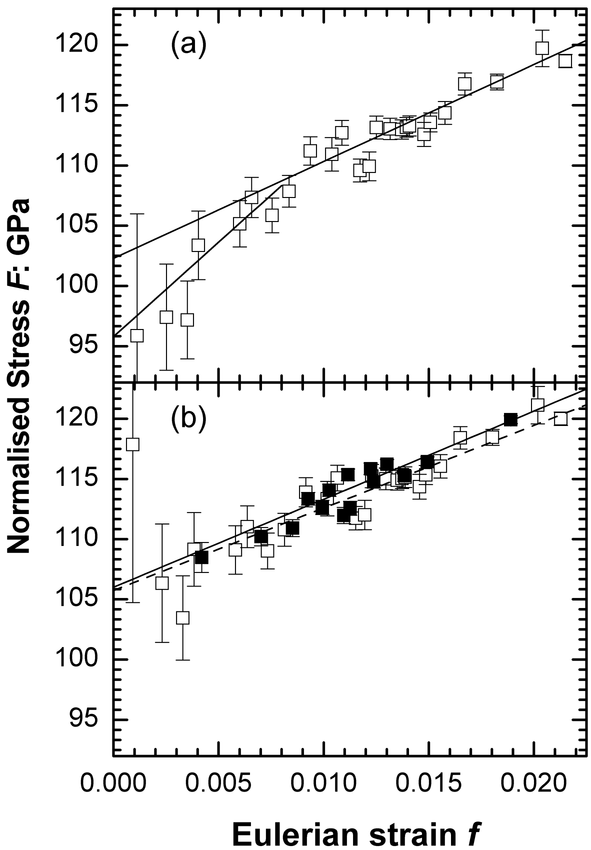

FIGURE 2. Plots of normalized stress against Eulerian strain for single-crystal compression data of orthoenstatite. (**a**) Data of Angel and Hugh-Jones (1994) plotted using V_0 = 832.9 Å^3, resulting in a low-pressure EoS with K_{T0} = 95.8 GPa. The same data are re-plotted as open symbols in (**b**) on the basis of a V_0 = 832.5 Å^3, showing that they are consistent with a single EoS with K_{T0} = 105.7 GPa (dashed line). The closed symbols are the new compression data that can be described by an indistinguishable EoS shown by the solid line (K_{T0} = 106.0 GPa).

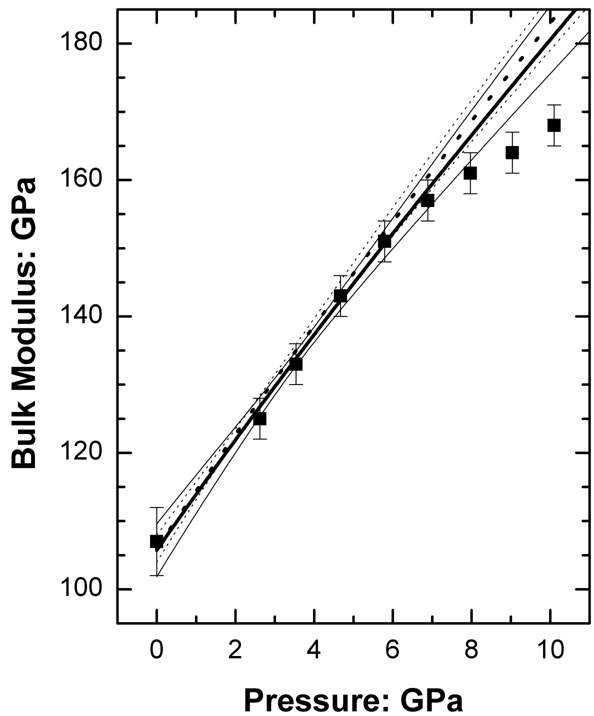

FIGURE 3. The in-situ ultrasonic measurements of the bulk modulus of orthoenstatite (symbols, Flesch et al. 1998). The solid line is the variation of K_T predicted by the EoS with K_{T0} = 105.7(1.9) GPa and K'_0 = 8.4(6) obtained from the refit of the single-crystal *P-V* data of Angel and Hugh-Jones (1994). The thin solid lines are 95% (±2 e.s.d.) confidence limits on these values. The bulk modulus obtained from the new single-crystal compression data, K_{T0} = 106.0(1.0) GPa and K'_0 = 8.6(4), is shown by the heavy dotted line and its 95% confidence limits as thin dotted lines.

become K_{T0} = 105.7(1.9) GPa and K'_0 = 8.4(6). Similar values of the EoS parameters, differing by less than 1 e.s.d., are obtained when various sub-sets of the data (without the room-pressure datum) are used in the least-squares fit. We conclude that the original fit was biased by an unidentified error in the experimental measurement of the room pressure volume. When plotted on a $f_E - F_E$ plot, calculated using the value of V_0 obtained from the new EoS fit, the experimental data fall on a straight line (Fig. 2b). A fit of a fourth-order Birch-Murnaghan EoS to the data results in a small increase in χ^2_w, indicating that an expansion of the EoS to fourth-order is not required to fit the data. Therefore, within the experimental uncertainties, the *P-V* data of Angel and Hugh-Jones (1994) can be described by a single third-order EoS, at least to 8.5 GPa. The new compression data obtained by single-crystal diffraction are also consistent with this interpretation. A separate fit to these 17 new data from two crystals yields K_{T0} = 106.0(1.0) GPa and K'_0 = 8.6(4) for a third-order EoS, and the data fall on a straight line in the $f_E - F_E$ plot (Fig. 2b). A fit of a fourth-order EoS to these new data results in an increase in χ^2_w from 2.8 to 3.0 and is therefore not justified.

Figure 3 shows a comparison of the values of K_T at high pressures derived from the refitting of the *P-V* data with those obtained from the in-situ ultrasonic measurements of Flesch et al. (1998). It is clear from this plot that both methods yield indistinguishable values of *K* and *K*' up to pressures of ~7 GPa. At higher pressures the ultrasonic values deviate to lower values of both *K* and *K*' than the EoS from the compression measurements. This curvature at high pressures was the reason for Flesch et al. (1998) suggesting that the EoS of orthoenstatite includes a significant fourth-order term. However, the curvature may instead be an experimental artifact, perhaps induced by use of a solid pressure medium in the ultrasonic measurements. Possible effects of a solid pressure medium include non-hydrostatic stresses on the sample itself and thus deviation of behavior from that obtained under hydrostatic conditions. Deviatoric stresses can also change the transition pressures of the materials used as pressure calibrants in the assembly, leading to over-estimates of sample pressures. If only the original travel time data reported by Flesch et al. (1998) up to 7 GPa are fitted by the method of Cook (1957) then EoS parameters of K_{T0} = 105.6(2.5) GPa and K'_0 = 8.2(7) are obtained.

Figure 4 illustrates the conclusion that the values of the isothermal room pressure bulk modulus of orthoenstatite obtained by reanalysis of previously reported compression data (Angel and Hugh-Jones 1994) and ultrasonic travel-time data (Flesch et al. 1998) are both in good agreement with the values obtained from Brillouin spectroscopy measurements (Weidner et al. 1978; Jackson et al. 1999). Combining the results of the various measurements yields best estimates of K_{T0} = 105.8(5) GPa and K'_0 = 8.5(3) for a third-order Birch-Murnaghan EoS. This general agreement between three measurement techniques confirms that orthoenstatite (and therefore probably orthopyroxenes in general) have "anomalously" high values of K'_0. A similarly high value was deduced by Chopelas (2000) from thermodynamic arguments. These high values of K'_0 are therefore not the result of experimental artifacts nor are they the result of fitting data over a limited pressure range.

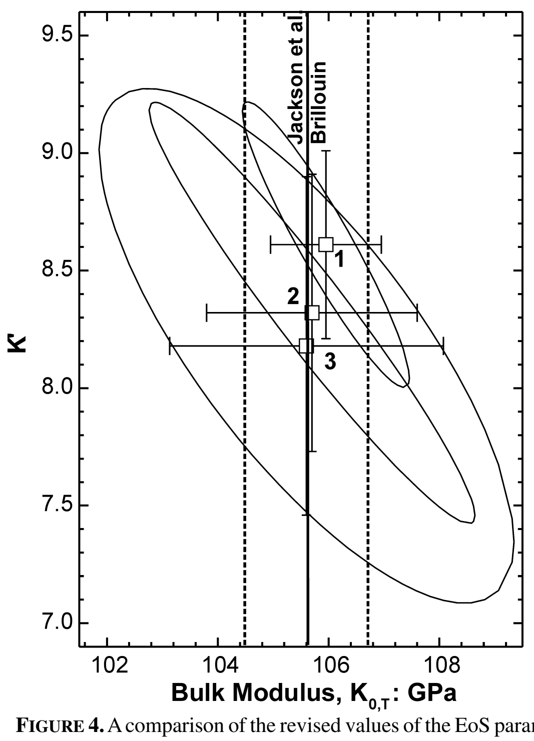

FIGURE 4. A comparison of the revised values of the EoS parameters K_{T0} and K'_0 obtained from various experimental techniques. The solid vertical line is the value determined by Jackson et al. (1999) with ±1 e.s.d. indicated by the broken vertical lines. The data points are (1) fit to the new X-ray data, (2) refit of the data of Angel and Hugh-Jones (1994), (3) fit of the ultrasonic data below 7 GPa of Flesch et al. (1998). Error bars are ±1 e.s.d. and the confidence ellipses centered on each data point are shown at the 68.3% level.

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