HUGONIOT EQUATION OF STATE OF PERiclase TO 200 GPa

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Abstract. New shock wave data on [100] oriented single crystal periclase covering the pressure range from 160 to 250 GPa suggest that MgO is described by a single Hugoniot up to 300 GPa, with no discrete phase transitions of volume change greater than 1.5%. For a third order finite strain fit, with K₀ constrained to its ultrasonically determined value of 182.7 GPa, the implied K' of 4.27 ± 0.24 is in agreement with ultrasonically determined value of 4.17 ± 0.14. The new data indicate a somewhat steeper Hugoniot than that suggested by previously published shock wave results under 120 GPa. A pre- viously published result at 250 GPa shows more compression in the light of the present data than would be expected for MgO in the B₁ structure, and may signal the onset of a phase transition, although we cannot confidently make this interpretation. If MgO forms an ideal solid solution with FeO, our data does not support the occurrence of a significant transition in magnesium-iron at lower mantle pressures.

1. Introduction

Magnesium oxide is a substance of considerable geophysical interest. It has played an important role in our thinking concerning the composition of the earth's lower mantle, from the early mixed oxides model of Birch (1942) to the more recent ideas proposing an equilibrium between ferromagnesian perovskite and magnesium-wadadeite (e.g., Liu, 1970). Because of this, as well as for other scientific and industrial reasons, periclase is an exceedingly well studied material.

There is a conspicuous lack of published data, however, in the high pressure regime above 300 GPa. The shock wave results of Carter et al. (1971) and the static high pressure results of Mao and Bell (1979) cover the range up to 120 GPa; there is then a large gap until a solitary datum of Altshuler et al. (1966) at 250 GPa. This is a large interval over which to extrapolate with confidence, and the Altshuler et al. datum was measured on an initially porous sample, making it more difficult to interpret. The pressure range above 120 GPa has been made all the more important by the discovery of a shock induced phase transition in wadsleyite, transition from 120 to 300 GPa (Carter et al., 1971). A shock-induced phase transition in periclase at high pressure could have significant geophysical implications. We present here the results of three shock wave experiments on single crystal periclase, covering the pressure range from 160 to 200 GPa, that data to previous ultrasonic and shock wave, and thermodynamic measurements, and briefly discuss possible geophysical implications.

2. Experimental

Samples of synthetic single crystal periclase (source: Norton Co.) on the order of 3 mm, in thickness (Table I), were mounted on tantalum driver plates and impacted by tantalum flyer plates launched by a two-stage light gas gun. The crystals were orientated such that the direction of impact was parallel to [100]. This orientation was more or less dictated by the physical nature of our samples; we note that a B₂,2 transition, which can be expected as a shock transition, might be observable at a lower pressure using a [111] orientation (Demarest et al., 1977; see Frisia et al., 1971, for evidence of this effect in NaCl).

The experimental setup used here was essentially the same as that described in detail by Vassiliou and Ahrens (1977, 1980a). Briefly, shock wave velocity was measured by use of arrival and buffer mirrors, whose change in reflectivity was monitored with an image-converter streak camera. Streak records were analysed by visual measuring photomicrographic prints, digitizing the arrival and fitting them by least squares, and, where appropriate, by performing microphotometer scans on the negatives. Most serious errors in the measurement of shock velocity. Two important sources of error here are hysteresis of targets caused by cross-talk in the image converter tube, and curvature of targets arising from projectile distortion at high velocities. The latter is particularly crucial in the case of the tantalum flyer plate relative to its impact testing (Kersting, 1977; Berne and Vashon, 1979). Projectile bowing is accounted for by appropriately fitting the curvature of the first arrival (Jackson and Ahrens, 1980a; Vassiliou and Ahrens, manuscript in preparation), rather than trusting the streak record, as is a set of parallel lines. Particle velocity is obtained by impedance matching (Altshuler et al., 1970), and the data are transformed to pressure-density space via the Riemann-Hugoniot relations. The error analysis is similar to that described by Jackson and Ahrens (1979). Formal errors in density (the largest error) are generally between 1 and 1.5% per cent.

3. Results and Discussion

The results of the three experiments are tabulated in Table 1, and plotted in Figs. 1 and 2 along with shock wave data from other investigators. Examining Fig. 1, we see that these present results are quite consistent with those of Carter et al. (1971), obtained at Los Alamos Scientific Laboratory (LASL). At least squares fit of the form

$$\log \sigma = C_0 + C_P \log (\rho)$$

to the LASL data, points yield $C_0 = 6.61 \pm 0.08 \text{ km/sec.}$, $C_P = 1.36 \pm 0.02$, to the LASL points and the present data, yields respectively $6.81 \pm 0.05$, $1.36 \pm 0.02$. These lines, which are very similar, are shown as curve 1. We note that $C_0$ here is somewhat lower than the value of 6.74 which would be expected from the ultrasonically determined value of K₀ = 182.7 ± 0.2 GPa (Jackson and Nixler, 1974). This difference is not consistent with other recent measurements, for example the value of 6.13 ± 0.7 obtained by Bonca and Graham (1981); see also Lipstein, 1970). As Carter et al. (1971) noted, this discrepancy is in the wrong direction to be explainable by simple effects. They proposed a phase change from the B₁ to the B₂ structure below 200 GPa as a possible explanation, but this is not consistent with the high-pressure range of Mao and Bell (1979). We have no alternative explanation. One more point to note in Fig. 1 is that these present data imply loss of a curvature in the 6-30 GPa range; thus might be expected from the LASL data alone (cf. curves 2 and 3, respectively). For all data in the figure and to LASL data only, respectively.

Fig. 2 shows a variety of equations-of-state curves in pressure-density space. All use third order polynomials (Klett-Mulligan).

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finite stress fits, according to the formulation of Davies (1973). Although higher order expressions might be physically more realistic at high pressures, it is not generally possible in practice to determine the parameters meaningfully for such fits. As we shall see, even the third order fits are difficult to fit stably when K₀ is not constrained by ultrasonic. We have performed two types of equation-of-state inversions: first, a two parameter inversion for K₀ and Kᵢ (see Appendix); and second, a simple constrained inversion for the single parameter Kᵢ₀, where in this case we have constrained K₀ to be equal to Jackson and Nieder's (1985) value. Results for the parameters in several cases of interest are summarized in Table 3. The errors given are formal standard errors of estimate. Only some of the fits are plotted in Fig. 2, partly because many of them approximately coincide. As Table 3 shows, the unconstrained inversions yield a relatively large variation in parameter values according to which points are fit. The two parameter Birch-Murnaghan inversion is somewhat less sensitive to the variation for the parameters in the shock wave equation of state (eq. 1). The constrained fits are more uniform. All yield Kᵢ₀ values close to those derived from ultrasonics; Jackson and Nieder's (1985) value for Kᵢ₀ is 4.17 ± 0.14. All in all, data from this study seem fairly consistent with those of Carter et al., but they do imply a certain steepening in the Hugoniot at light pressure (compare curves 1 and 2 with curve 3). We might note that Fosdick's (personal communication) has done theoretical work suggesting a steeper Hugoniot than the LASL curve at high pressures.

In this light, the 258 GPa datum of Afzal-i-Hussaini et al. (1965) raises some interesting possibilities. Viewed superficially, it may seem quite consistent with the lower pressure results. We must remember, however, that this datum represents an experiment conducted on an initially porous sample. Afzal-i-Hussaini et al.'s reported initial density is 2.425 g./cc., thus a porosity of 4.4 per cent. To view this datum more meaningfully, then, we must apply some correction for the inevitable porosity incurred by an initially porous sample under shock. This phenomenon is discussed in detail by Zel'dovich and Raizer (1967). We may apply Afzal-i-Hussaini et al.'s equation (1):

$$ P₁ = P₀(\frac{1}{(\rho₀/\rho_₁)) \left(1 - \frac{2}{(\gamma - 1)} \right)$$

where P₀ is crystal pressure; P₁ is porosity pressure; ρ₀ and ρ₁ are respectively density, initial crystal density, and initial porosity density; and γ is the high pressure (crumpling) parameter. T must somehow be obtained from T₀, the zero pressure value, assuming some form for the volume dependence. An empirical relationship of the form

$$ T(\rho) = T₀(\rho₀/\rho)^{p}$$

is often used (Zel'dovich, 1979). Carter et al. (1971) present various data, as well as the single crystal data shown in Figs. 1 and 2; however, some information does exist on the volume dependence of T in MgO. There is considerable scatter in their data, but eq. 3 is consistent with their results. The vertical bar in Fig. 2 shows a range for the corrected positions of Afzal-i-Hussaini et al.'s datum for zero pressure germanium parameters from 1.0 to 1.5, and u₁=0.4 (Available data suggests a best value of about 1.5 for T₀ (Zel'dovich et al., 1977)). Afzal-i-Hussaini et al.'s corrected datum appears to indicate more compression than would be expected for MgO in the H₁ structure. It is deeper by about three per cent than the predicted value according to curve 3, and about two percent compared with the predicted value from curve 2; these being respectively the unconstrained and constrained fits to all data.
under 200 GPa. Cautiously, we might consider this a significant deviation, and a possible indicator of a transition to a denser phase. In this case, however, great caution must be exercised before such an interpretation is made. We do not know the experimental error associated with Afsahade et al.'s datum. We note, also, that Afsahade et al.'s porosity deviates insignificantly from curve 4, which represents the highest density error bound to the constrained fit. One interpretation, then, is that even without error bars, Afsahade et al.'s datum lies marginally within the scatter of the lower pressure points.

In any case, one fairly certain and important conclusion is that up to 200 GPa there is no phase transition in MgO involving a density change greater than 1.5 per cent or so. Though a phase change may be occurring with a volume change small enough to be undetectable by this method (systematics tell us that it is indeed possible with certain transitions, e.g., ZnO to ZnI (Jamieson, 1977)), we can state with some confidence that there is no transition comparable to that observed in graphite. We note in this connection that the results are consistent with this; they fall to the left of the upper limit in Fig. 2 and do not display the anomalous behavior sometimes associated with phase transitions (cf. the release data for C60 of Jonat and Ahrens, 1993a, Ahrens and Redd, unpublished results). By itself, the absence of a large transition in MgO below 200 GPa tends to imply that contrary to the initial assertions of Jameson and Ahrens (1986a), the wurtzite phase change is probably not directly important to the lower mantle, where pressures are less than about 100 GPa. If MgO forms an ideal solid solution with FeO, a significant phase change in [MgO,FeO]0, with x 0.5, in equilibrium with lower mantle composition [MgO,FeO]0 (Vapi et al., 1979), is not supported by the present data. If the FeO transition is a simple structural one, this may simply be because the volume change decreases smoothly across the solid solution series (w-zw MgO). Also possible, however, is that we are dealing with a phenomenon quite localized to the iron rich end. The nature of the FeO transition is still uncertain, and recent static pressure data (Zou et al., 1989) indicate that it may be a far more complex process than originally proposed (e.g., for Fe 180 and hypothesis of Jameson and Ahrens, 1985).

4. summary of Conclusions

(1.) New shock wave data on MgO suggest that this material is not preserved by a single Hugoniot up to 200 GPa, with no explosive phase transitions of volume change greater than 1.5-1.5 per cent.

(2.) For a third order finite strain fit, with K0 compressed to its ultrametamorphic determined value of 207.7 GPa, the refined K0 of 247.0 ± 24 in agreement with the ultrametamorphic determined value of 4.17 ± 0.16.

(3.) The new data suggest a somewhat stiffer Hugoniot than do existing data under 150 GPa. A 256 GPa datum obtained by Afsahade et al. (1995) shown, when corrected for initial porosity, more compression by roughly two per cent than most of the previous data. In addition, it is consistent with our data and the data of Carter et al. (1971). This data may signal the onset of a phase transition, but we cannot confidently make this interpretation.
Appendix

Finding the optimum Θ and Θ' from Hugoniot data can, with certain assumptions, be reduced to a simple two-parameter biaxial state equation problem. In the Birch-Murnaghan case (see Davies, 1973), we put
\[ x = (\mu / \rho)^{1/3} \]
\[ \xi = (3/8)(4 - \xi) \]  (A1)
The Hugoniot where there is no initial porosity is given by
\[ P_{H} = P_{0}(\xi^{1/3} + 1) \{1/2(3/2)) - 1/2(3/2)) \} \]  \[ - (1/2) \]  (A2)

The isentropic pressure and energy \( P_{H} \) and \( E_{H} \) respectively given by
\[ P_{H} = (2/3)\xi(1 - \xi^{2}) \{1 + (1 - \xi^{2}) \} \]  \[ - (1/2) \]  (A3)
\[ E_{H} = (2/3)\xi(1 - \xi^{2}) \{1 + (1 - \xi^{2}) \} (2 + 1/6) \]  \[ - (1/2) \]  (A4)

This is for the general case where we may have a phase transition; all quantities refer to the high pressure phase except \( P_{H} \), the low pressure phase initial density. \( \xi = \) is the mass density.

Generally there is not enough anisotropy in a density-pressure Hugoniot data set to invert for all the unknowns, even in the ideal order case. We must replace the number of unknowns by fixing \( \xi \) and assuming a volume dependence for \( P \). In the case of SiO, as discussed in the text, elastic data suggest \( \xi = 1.5829 \). In any case, physically reasonable, variations in \( \xi \) do not have a significant effect on the estimated \( P_{H} \).

Jeansou and Albers (1980b) transform (A1) to a form
\[ \psi(P_{H}, \rho_{0}, \alpha) = \psi_{0} + \psi_{1}(\alpha) \]  (A5)

where \( \psi \) and \( \chi \) are complicated functions, and solve for \( P_{H} \) and \( E_{H} \) by least squares. In this study we use a slightly different, perhaps more standard, approach: Taking \( \psi_{0} \) and \( \psi_{1} \) as initial guesses for the parameters, we compute \( \psi_{0} \) from (A2). We then write
\[ \psi(P_{H}, \rho_{0}, \alpha) = \psi_{0} + \psi_{1}(\alpha) \]  (A6)
where the partial derivatives are found analytically from (A1) and (A4), and
\[ \Delta P_{H} = P_{H} - P_{0} - \Delta \psi_{0} \]  (A7)
\[ \Delta E_{H} = E_{H} - E_{0} - \Delta \psi_{0} \]  (A8)

We solve for \( P_{0} \) and \( \Delta \psi_{0} \) by least squares, obtain new guesses for the parameters, and iterate until convergence is obtained.

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