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 200 GPa suggest that MgO is described by a single Hugoniot up to 200 GPa, with no displacive phase transitions of volume change greater than 1-1.5 per cent. For a third order finite strain fit, with K_0 constrained to its ultrasonically determined value of 162.7 GPa, the implied K_0' 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 previously published result at 258 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 magnesiowustite 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 (1952) to the more recent ideas propounding an equilibrium between ferromagnesian perovskite and magnesiowustite (e.g. Liu, 1979). 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 100 GPa. The shock wave results of Carter et al. (1971) and the static high pressure data of Mao and Bell (1979) cover the range up to 120 GPa; there is then a large gap until a solitary datum of Al'tshuler et al. (1965) at 258 GPa. This is a large interval over which to extrapolate with confidence, and the Al'tshuler et al. datum was moreover obtained 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 wustite of volume change four per cent or greater (Jeanloz and Ahrens, 1980a); a similar 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, relate these data to previous ultrasonic, 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 1) were mounted on tantalum driver plates and impacted by tantalum flyer plates launched by a two-stage light gas gun. The crystals were oriented 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 B1/B2 transition, which can be regarded as a shear transformation, might be observable

at a lower pressure using a $\{111\}$ orientation (Demarest et al., 1977; see Fritz 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 Jeanloz and Ahrens (1977, 1980a). Briefly, shock 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 visually measuring photographic prints, digitizing the arrivals and fitting them by least squares, and, where appropriate, by performing microphotometer scans on the negatives. The most serious errors are in the measurement of shock velocity. Two important sources of error here are fuzziness of arrivals caused by crosstalk in the image converter tube, and curvature of arrivals arising from projectile distortion at high velocities. The latter is presumably caused by the inertia of the tantalum flyer plate relative to its lexan casing (Bernier, 1977; Bernier and Valadon, 1979). Projectile bowing is accounted for by appropriately fitting the curvature of the first arrival (Jeanloz and Ahrens, 1980a; Vassiliou and Ahrens, manuscript in preparation), rather than treating the streak record as a set of parallel lines. Particle velocity is obtained by impedance matching (McQueen et al., 1970), and the data are transformed to pressure-density space via the Rankine-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 2, and plotted in Figs. 1 and 2 along with shock wave data from other investigators. Examining Fig. 1, we see that the 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

$$U_s = C_0 + sU_p \qquad (1)$$

to the LASL points only yields $C_0 = 6.61 \pm 0.06$ km./sec., $s = 1.36 \pm 0.03$; to the LASL points and the present data, it yields respectively 6.61 ± 0.05, 1.36 ± 0.02. These lines, which are very similar, are drawn 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 $K_0 = 162.7 \pm 0.2$ GPa (Jackson and Niesler, 1981). (This value is compatible with other recent measurements, for example the value of 162.1 ± 1.7 obtained by Bonczar and Graham, 1981; see also Spetzler, 1970). As Carter et al. (1971) noted, this discrepancy is in the wrong direction to be explainable by rigidity effects. They proposed a phase change from the B1 to the B2 structure below 20 GPa as a possible explanation, but this is not consistent with the later static results of Mao and Bell (1979); we have no alternative explanation. One more point to note in Fig. 1 is that the present data imply less of a curvature in the Us-Up Hugoniot than might be expected from the LASL data alone (cf. curves 2 and 3, quadratic fits to all data in the figure and to LASL data only, respectively).

Fig. 2 shows a variety of equation-of-state curves in pressure-density space. All are third order Eulerian (Birch-Murnaghan)

Table 1. Experimental Conditions

Shot #	Flyer/ Driver	Buffer Material	Impact Velocity, km./sec.	Bulk Density, g./cc.	Archim. Density, g./cc.	Sample Thckns., mm.	Buffer Thckns., mm.
LGG070	Ta	FQ[1]	5.585 (0.05)[2]	3.553 (0.003)	3.580 (0.003)	2.940 (0.0025)	1.900 (0.0025)
LGG102	Ta	FQ	6.01 (0.01)	3.569 (0.003)	3.582 (0.003)	3.114 (0.0025)	1.936 (0.0025)
LGG072	Ta	FQ	6.48 (0.06)	3.554 (0.003)	3.585 (0.003)	3.499 (0.0025)	1.863 (0.0025)

[1] Fused Quartz
[2] Standard error

finite strain fits, according to the formulation of Davies (1973). Although higher order expansions 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 case is difficult to fit stably when K_0 is not constrained by ultrasonics. We have performed two types of equation-of-state inversions: first, a two parameter inversion for K_0 and K_0 ' (see Appendix); and second, a simple constrained inversion for the single parameter K_0', where in this case we have constrained K_0 to be equal to Jackson and Niesler's (1981) value. Results for the parameters in several cases of interest are summarised 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 stable than the inversion for the parameters in the shock wave equation of state (eq. 1). The constrained fits are rather more uniform. All yield K_0' values consistent with those derived from ultrasonics: Jackson and Niesler's (1981) value for K_0' is 4.17 ± 0.14. All in all, data from this study seem fairly compatible with those of Carter et al., but they do imply a certain steepening in the Hugoniot at higher pressure (compare curves 1 and 2 with curve 3). We might note that Bukowinski (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 Al'tshuler 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. Al'tshuler et al.'s reported initial density is 3.425 g./cc., thus a porosity of 4.4 per

cent. To view this datum more meaningfully, then, we must apply some correction for the irreversible heating incurred by an initially porous sample under shock. This phenomenon is discussed in detail by Zel'dovich and Raizer (1967). We may apply Al'tshuler et al.'s equation (1):

$$P_c = P_p(h - (\rho/\rho_0))/(h - (\rho/\rho_c))$$
$$h = 1 + (2/\Upsilon) \qquad (2)$$

where P_c is crystal pressure; P_p is porous pressure; ρ, ρ_c, and ρ_0 are respectively dynamic density, initial crystal density, and initial porous density; and Υ is the high pressure Gruneisen parameter. Υ must somehow be obtained from Υ_0, the zero pressure value, assuming some form for the volume dependence. An empirical relationship of the form

$$\Upsilon(\rho) = \Upsilon_0(\rho_0/\rho)^n \qquad (3)$$

is often used (Jeanloz, 1979). Carter et al. (1971) present porous data, as well as the single crystal data shown in Figs. 1 and 2; hence, some information does exist on the volume dependence of Υ in MgO. There is considerable scatter in their data, but n=1 in eq. 3 is consistent with their results. The vertical bar in Fig. 2 shows a range for the corrected positions of Al'tshuler et al.'s datum for zero pressure Gruneisen parameters from 1.0 to 1.5, and n=1. (Available data suggests a best value of about 1.3 for Υ_0 (Touloukian et al., 1977)).

Al'tshuler et al.'s corrected datum appears to indicate more compression than would be expected for MgO in the B1 structure. It is denser by about three per cent than the predicted value according to curve 1, and about two percent compared with the predicted value from curve 2, these curves being respectively the unconstrained and constrained fits to all data

Table 2. Results
Standard Errors in Parentheses

| Shot #	Hugoniot State				Release State			
	Shock Velocity km./sec.	Particle Velocity km./sec.	Pressure GPa	Density g./cc.	Shock Velocity km./sec.	Particle Velocity km./sec.	Pressure GPa	Density g./cc.
LGG070	11.70 (0.17)	3.842 (0.04)	159.7 (2.3)	5.29 (0.05)	9.49 (0.14)	5.28 (0.09)	110.4 (3.5)	4.33 (0.17)
LGG102	12.33 (0.27)	4.11 (0.02)	180.7 (3.0)	5.35 (0.07)	9.75 (0.25)	5.45 (0.16)	117.1 (6.4)	4.65 (0.21)
LGG072	12.64 (0.15)	4.44 (0.05)	199.3 (2.7)	5.48 (0.05)	10.39 (0.13)	5.85 (0.08)	133.8 (3.4)	4.70 (0.14)
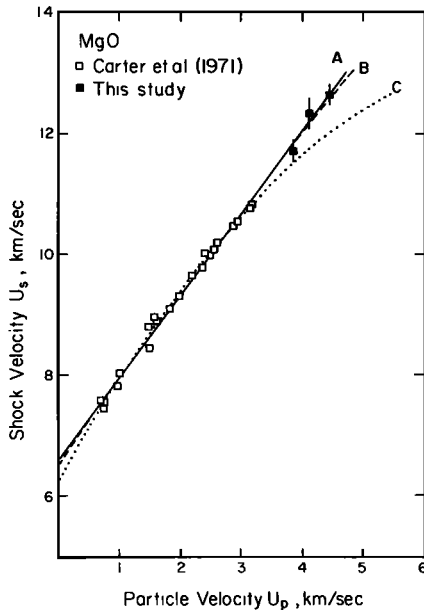
Figure 1. Shock wave data for MgO. Curve A = Linear fit to all data in figure; coincides approximately with linear fit to LASL data only (Carter et al., 1971) (eq. (1) of text ff.). Curve B = Quadratic fit to all data in figure. Curve C = Quadratic fit to LASL data only.

under 200 GPa. Ordinarily, 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 Al'tshuler et al.'s datum. We note, also, that Al'tshuler et al.'s point deviates insignificantly from curve 4, which represents the highest density error bound
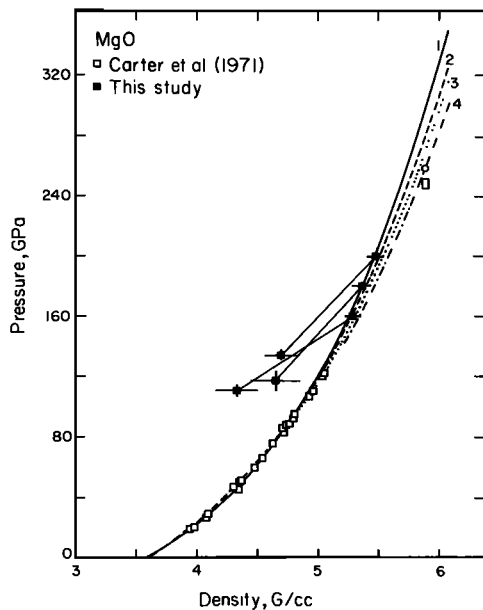

Figure 2. Pressure-Density Hugoniot equations of state (Table 3.) Open circle = Al'tshuler et al. (1965) datum for 4.4 per cent porous MgO. Open rectangle = Reasonable range of pressures when Al'tshuler et al. datum is corrected for porosity. Curve 1 = Unconstrained 3rd order fit to LASL data plus present data, Curve 2 = Constrained fit to same, Curve 3 = Constrained fit to LASL data only, Curve 4 = Highest density error bound to curve 2.

Table 3. Equation of State

| | Parameters (standard errors in parentheses) | | |
| | Unconstrained | | Constrained, K_0=162.7 GPa |
Data Included	K_0, GPa	K_0'	K_0'
LASL only	165.7 (3.7)	4.1 (0.12)	4.19 (0.16)
LASL plus present data	149.2 (3.7)	4.8 (0.13)	4.27 (0.24)
All, including Al'tshuler et al.[1]	169.8 (5.27)	4.03 (0.12)	4.23 (0.29)

[1] Corrected for porosity using $\rho T=1.32\rho_0$

to the constrained fit. One interpretation, then, is that even without error bars, Al'tshuler 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 so small as to be undetectable by this method (systematics tell us that this is possible with certain transitions, e.g. B1 to B2 (Jamieson, 1977)), we can state with some confidence that there is no transition comparable to that observed in wustite. We note in this connection that the release data are consistent with this result; they all lie to the left of the Hugoniot in Fig. 2 and do not display the anomalous behavior sometimes associated with phase transitions (cf. the release data for CaO of Jeanloz and Ahrens, 1980a; Ahrens and Watt, unpublished results). By itself, the absence of a large transition in MgO below 200 GPa tends to imply that contrary to the initial suspicions of Jeanloz and Ahrens (1980a), the wustite phase change is probably not directly important to the lower mantle, where pressures are less than about 130 GPa. If MgO forms an ideal solid solution with FeO, a significant phase change in $(Mg_x Fe_{1-x})$ O, with x⩾ 0.6, in equilibrium with lower mantle composition $(Mg,Fe)SiO_3$ (Yagi 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 towards 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., 1980) indicate that it may be a far more complex process than originally proposed (e.g. the B1 — B2 hypothesis of Jeanloz and Ahrens, 1980a).

4. Summary of Conclusions

(1.) New shock wave data on MgO suggest that this material is described by a single Hugoniot up to 200 GPa, with no displacive phase transitions of volume change greater than 1-1.5 per cent.

(2.) For a third order finite strain fit, with K_0 constrained to its ultrasonically determined value of 162.7 GPa, the implied K_0' of 4.27± 0.24 is in agreement with the ultrasonically determined value of 4.17 ± 0.14.

(3.) The new data suggest a somewhat steeper Hugoniot than do existing data under 120 GPa. A 258 GPa datum obtained by Al'tshuler et al. (1965) shows, when corrected for initial porosity, more compression by roughly two per cent than might be expected for MgO in the B1 structure on the basis of our data and the data of Carter et al. (1971). This may signal the onset of a phase transition, but we cannot confidently make this interpretation.

Appendix

Finding the optimum K_0 and K_0' from Hugoniot data can, with certain assumptions, be reduced to a simple two-parameter least squares problem. In the Birch-Murnaghan case (see Davies, 1973), if we put

$$x = (\rho/\rho_c)^{1/3} \tag{A1}$$

$$\xi_1 = (3/4)(4 - K_0')$$

the Hugoniot where there is no initial porosity is given by

$$P_H = (E_s - (P_s/\rho T) + E_{TR}) \left\{ (1/2)(1/\rho_{c1} - 1/\rho) - 1/\rho T \right\}^{-1} \tag{A2}$$

with the isentropic pressure and energy P_s and E_s respectively given by

$$P_s = (3/2)K_0(x^7 - x^5)[1 + (1-x^2)\xi_1] \tag{A3}$$

$$E_s = (9/2)(K_0/\rho_c)\{(1+\xi_1)(x^4/4 - x^2/2 + 1/4) \\ - \xi_1(x^6/6 - x^4/4 + 1/12)\} \tag{A4}$$

This is for the general case where we may have a phase transition; all quantities refer to the high pressure phase except ρ_{c1}, the low pressure phase initial density. E_{TR} is the transition energy.

Generally there is not enough sensitivity in a pressure-density Hugoniot data set to invert for all the unknowns, even in the third order case. We must reduce the number of unknowns by fixing T_0 and assuming a volume dependence for T. In the case of MgO, as discussed in the text, available data suggest $\rho T = 1.32\rho_0$. In any case, physically reasonable variations in T do not have a significant effect on the calculated P-ρ Hugoniot.

Jeanloz and Ahrens (1980b) transform (A3) to a form

$$Y(x, E_{TR}, \rho_{c1}, \rho) = K_0 + (K_0\xi_1)X(x) \tag{A5}$$

where Y and X are complicated functions, and solve for K_0 and $(K_0\xi_1)$ by least squares. In this study we use a slightly different, perhaps more standard, approach. Taking K_0^0 and ξ_1^0 as initial guesses for the parameters, we compute P_H^0 from (A2.). We then write

$$P_H - P_H^0 = (\partial P_H/\partial K_0)\Delta K_0 + (\partial P_H/\partial \xi_1)\Delta \xi_1 \tag{A6}$$

where the partial derivatives are found analytically from (A1)—(A4), and

$$\Delta K_0 = K_0 - K_0^0 \\ \Delta \xi_1 = \xi_1 - \xi_1^0 \tag{A7}$$

We solve for ΔK_0 and $\Delta \xi_1$ by least squares, obtain new guesses for the parameters, and iterate until convergence is obtained.

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