GEOPHYSICAL RESEARCH LETTERS, VOL. 9, NO. 2, PAGES 127-130, FEBRUARY 1982

THE EQUATION OF STATE OF $Mg_{0.6}Fe_{0.4}O$ TO 200 GPa

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Abstract. New Hugoniot data on polycrystalline (avg.porosity 6.9%) samples of the magnesiowustite $Mg_{0.6}Fe_{0.4}O$ are presented, covering the pressure range up to 200 GPa. When our data are fit by a single 3rd order Eulerian Hugoniot with K_0 constrained to its ultrasonic value of 161.5 GPa, the required isentropic pressure derivative K_0' is 4.37 +/- 0.37. This value is significantly lower than the ultrasonic one of 6.18; existing isothermal compression data, however, are in agreement with our value rather than the ultrasonic one. Our data are adequately explained without phase transitions. There is some marginal evidence for a possible phase transition around 120 GPa. If such a transition indeed occurs it is probably of small volume change compared to the transition observed in FeO; we place an extreme upper bound of 3% on the density change such a transformation could involve and still be consistent with the data. Contrary to earlier hypotheses, we believe that a phase transition in magnesiowustite is not a likely explanation of the seismic effects in the D'' region of the lower mantle. The wustite transition may be a more complex phenomenon than initially supposed-- perhaps an effect of nonstoichiometry localized to the iron-rich end of the solid solution series.

1. Introduction

Current thought concerning the composition of the Earth's lower mantle involves magnesiowustite as a possible phase, in equilibrium with ferromagnesian perovskite (e.g., Yagi et al, 1979). The proportion of magnesiowustite in a simple model lower mantle could vary from zero for a pure pyroxene stoichiometry to a mole fraction of 1/2 for pure olivine.

Jeanloz and Ahrens (1980) reported a major shock-induced phase transition in $Fe_{0.94}O$ at ~ 75 GPa. They speculated that a similar transformation in MgO at pressures as high as 170 GPa could, given solid solution behavior, imply a transition in lower-mantle composition magnesiowustite, perhaps explaining in part the observed seismic anomalies in the D'' region. Such anomalies include a non-increasing velocity profile with depth and seismic wave scattering, with possible heterogeneities (e.g. Cleary, 1974). Recently, a seismic phase preceding ScS has been observed at distances beyond 70°, indicating the presence of a discontinuity in the region (Lay and Helmberger, 1981).

Since then, there has been considerable discussion in the literature about the nature and effects of a possible phase transition in magnesiowustite. Navrotsky and Davies (1981) prefer nickel arsenide as a structure for the high pressure phase of FeO rather than the B2 structure favored by Jeanloz and Ahrens (1980). Jackson and Ringwood (1981) consider both a change to the NiAs structure and an electronic transition more likely than a B1 → B2 transformation. Vassiliou and Ahrens (1981) have studied periclase under shock compression to 200 GPa, and found no phase transformation comparable to that observed in wustite. Thus a direct examination of the equation of state of an intermediate composition magnesiowustite has become necessary. In this paper we present new shock wave data for the Hugoniot of $Mg_{0.6}Fe_{0.4}O$ to 200 GPa. This composition of magnesiowustite was chosen both because it is near the middle of the solid solution series and because partitioning calculations (Yagi et al, 1979; Watt and Ahrens, 1981) indicate that it might be close to the composition actually expected for magnesiowustite in the lower mantle.

2. Experimental

The samples of magnesiowustite used in this study are from a group of samples prepared and studied ultrasonically by Bonczar and Graham (1981). As described in that paper, the samples were prepared by reacting MgO, Fe_2O_3, and Fe to obtain a powder which was then hot-pressed. Bonczar and Graham (1981) characterised the samples using both microprobe and wet chemical analyses; the former yielded a composition of $Mg_{0.6}Fe_{0.4}O$, and the latter revealed no appreciable non-stoichiometry. Our own microprobe analyses yielded an average composition of $Mg_{0.6}Fe_{0.4}O$, with a range from $Mg_{0.57}$ to $Mg_{0.63}$. The hot-pressed samples used here had an average bulk density of 4.257 g/cc, suggesting an average porosity of 6.9% by comparison with the X-ray density of 4.57 g/cc. Porosity was on a scale of 10-50 microns, and the discrepancy between the X-ray density and the Archimedean densities (Table 1) shows that it was not all interconnected.

Details of how the shock wave data are obtained and reduced will not be given here; a description can be found in Jeanloz and Ahrens (1980). As in the study of Vassiliou and Ahrens (1981), crosstalk in the image- converter tube of the streak camera caused fuzziness in the arrivals, and was an important source of error in the measurement of shock velocity in the light gas gun (LGG) shots. Also as in previous studies, projectile distortion at high velocities was a source of error (here, in shots LGG081 and LGG091). Shots LGG085 and LGG094, both made at high velocity using Al-2024 flyer and driver plates, yielded records with some spurious arrivals, which we believe represented small pieces of material spalling off the projectile.

3. Results and Discussion

The raw results are tabulated in Table 1., and upon correction for initial porosity (see e.g. Al'tshuler et al., 1965) are plotted in Figs. 1 and 2. No data exist on the thermal expansion of our material, so we had to assume a value for the zero pressure Gruneisen parameter γ_0. We obtained a value of $\gamma_0 = 1.5$ to use in the correction of the data to crystal density by suitably averaging (McQueen, 1968) the available values of 1.32 for MgO and 1.63 for FeO (see Touloukian et al., 1966, for thermal expansion data on these materials). We assumed $\rho\gamma$ = constant.

The ultrasonic data for $Mg_{0.6}Fe_{0.4}O$ have a relatively large scatter. Bonczar and Graham (1981) obtained a bulk modulus K_0 of 161.5 +/- 8 GPa and a pressure derivative K_0' (isothermal) of 6.18 +/- 0.16 for an aliquot from the same group whence our samples were derived. On an aliquot from another group of only slightly different composition ($Mg_{0.585}$), they obtained K_0 = 168.7 +/- 11.3 GPa, and did not report K_0'. Jackson et al (1978) did not study any samples of our particular composition, but interpolation

Paper number 1L1853.
0094-8276/82/001L-1853$01.00

Table 1 : $Mg_{0.6}Fe_{0.4}O$ Shock Wave Data

Standard Errors Listed Underneath Measurements

EXPERIMENTAL CONDITIONS						HUGONIOT STATE				RELEASE STATE			
Shot #	Flyer/ Driver Mater.	Buffer Mater. (*)	Bulk Dens. (g/cc)	Arch. Dens. (g/cc)	Impact Veloc. (km/s)	Shockwave Veloc. (km/s)	Particle Veloc. (km/s)	Pressure (GPa)	Density (g/cc)	Shockwave Veloc. (km/s)	Particle Veloc. (km/s)	Pressure (GPa)	Density (g/cc)
486	W	L	4.264	4.416	2.09	7.34	1.55	48.6	5.41				
			0.003	0.004	0.01	0.07	0.008	0.4	0.02				
495	W	L	4.256	4.413	2.39	7.70	1.76	57.8	5.52				
			0.003	0.004	0.02	0.1	0.016	0.8	0.03				
LGG094	Al	FQ	4.233	4.368	5.45	8.57	2.30	83.6	5.79	6.12	3.16	42.5	5.25
			0.004	0.005	0.03	0.32	0.04	1.7	0.12	0.3	0.19	4.6	0.3
LGG085	Al	FQ	4.265	4.408	6.47	9.06	2.76	106.5	6.13	7.32	3.92	63.2	5.15
			0.004	0.005	0.02	0.3	0.04	1.9	0.13	0.3	0.19	5.6	0.4
LGG087	Cu	FQ	4.259	4.408	4.92	9.23	2.99	117.5	6.30	7.85	4.25	73.6	5.13
			0.004	0.005	0.01	0.12	0.01	1.1	0.05	0.11	0.07	2.2	0.15
LGG098	Cu	FQ	4.241	4.368	5.45	9.51	3.33	134.4	6.52	8.80	4.85	94.0	4.75
			0.004	0.004	0.04	0.19	0.02	1.9	0.09	0.18	0.1	4.0	0.32
LGG073	Ta	FQ	4.274	4.416	5.34	10.19	3.62	157.5	6.62	9.30	5.16	105.8	5.07
			0.001	0.004	0.04	0.19	0.03	2.6	0.09	0.17	0.1	4.0	0.27
LGG081	Ta	FQ	4.274	4.404	5.94	10.63	4.02	182.6	6.88	10.16	5.71	127.8	5.07
			0.003	0.005	0.01	0.17	0.02	2.1	0.08	0.16	0.1	4.3	0.27
LGG091	Ta	FQ	4.246	4.372	6.34	11.03	4.29	200.8	6.94	10.33	5.81	132.4	5.62
			0.001	0.005	0.01	0.17	0.02	2.3	0.09	0.16	0.1	4.3	0.21

(*) L=Lexan, FQ=Fused Quartz

between compositions they did study yields a value of roughly 168 GPa, which is within Bonczar and Graham's (1981) range.

The shock data are not completely compatible with the ultrasonic results. We fit our data with a Hugoniot calculated from a Birch-Murnaghan principal isentrope, and hence parameterized by the isentropic values K_0^S and $K_0^{S'}$ of the bulk modulus and its pressure derivative. The two parameter least-squares fit (Vassiliou and Ahrens, 1981) yields K_0^S = 196.0 +/- 14.6 GPa, and $K_0^{S'}$ = 3.44 +/- 0.25. The Hugoniot is represented by Curve 1 in Fig.2, with the highest and lowest density error bounds respectively represented by curves 1(a) and 1(b). These bounds are calculated by using extremal values of the parameters within their error range. That K_0 and K_0' from shock waves are respectively higher and lower than the corresponding values from ultrasonics is in keeping with the trend observed in several materials by Ruoff and Chhabildas (1977, as cited by Davison and Graham, 1979). What is perhaps a more significant discrepancy is that when K_0 is constrained to the Bonczar and Graham (1981) value of 161.5 GPa, the K_0' required by our data is 4.37 +/- 0.37 (this constrained fit is drawn as Curve 2 in Fig. 2), significantly lower than the ultrasonic value of 6.18. The discrepancy is much too large to be explained by the fact that the ultrasonic value is isothermal and our value is isentropic. We note that there is a similar discrepancy in the case of FeO. Bonczar and Graham obtain 19.07 +/- 0.25 for K_0', whereas the shock wave study of Jeanloz and Ahrens (1980) yields K_0' = 3.2 +/- 0.3. with K_0 constrained to its ultrasonic value. For FeO, part of the explanation may lie in a possible pressure-temperature dependence (unknown at present) of the non-stoichiometry (Bonczar and Graham,1981). This explanation is not likely to apply to our case, however, as our magnesiowustite is stoichiometric. The static compression data of Rosenhauer et al (1976) for $Mg_{0.6}Fe_{0.4}O$ are more in agreement with our results than with the ultrasonic ones: when fit with a Birch equation, with K_0'=4, they yield a K_0 of 157 GPa. In other words, a fit to the isothermal compression data with a K_0 close to its ultrasonic value requires a significantly lower value of K_0' than that measured ultrasonically-- as is the case with our data. We note that the uncertainties in the ultrasonic K_0' may be larger than those quoted by Bonczar and Graham (1981), as K_0' is a fairly difficult and indirect measurement; this could provide the explanation for the mismatch.

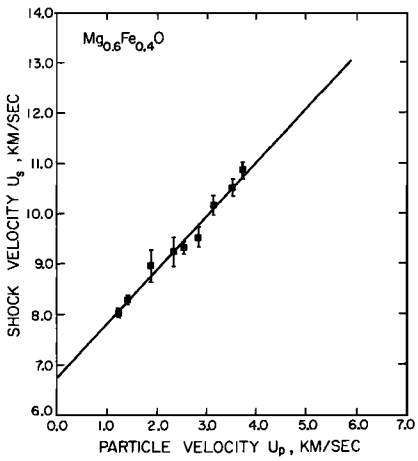

Fig. 1 Shock wave data for $Mg_{0.6}Fe_{0.4}O$, corrected for porosity with γ_0 = 1.5, $\rho\gamma$ = constant. A linear least squares fit (shown) of the form $U_s = C_0 + sU_p$ yields C_0 = 6.73 +/- 0.16 km/sec, s = 1.08 +/- 0.06.

Because of the apparent phase transition in FeO and the possibility of a transition in MgO above 200 GPa (Vassiliou and Ahrens, 1981; small volume transformations may also be possible below 200 GPa), we critically examine our data for evidence of a high pressure-high temperature phase transformation in $Mg_{0.6}Fe_{0.4}O$. The error of estimate of K_0 from the shockwave data is rather large; such scatter in the data might lead one to suspect the possibility of a phase transition. Before making this interpretation, however, one should note that the error in the ultrasonic determination is similarly large.

There does appear to be a slight density shift around 120 GPa; it is difficult to say whether or not this is a real feature. Unfortunately, as noted in Section 2, the data which lie in this pressure region are among the least reliable. We are inclined to conclude that our data do not offer positive evidence of a phase transformation; we note in this connection that the release data shown in fig. 2 lie at a lower density than the Hugoniot, and hence do not display the anomalous behavior sometimes associated with mixed-phase regions (see, for example, the CaO data of Jeanloz and Ahrens, 1980). We will proceed, however, to place bounds on how large such a hypothetical transformation could be and still be consistent with the data.

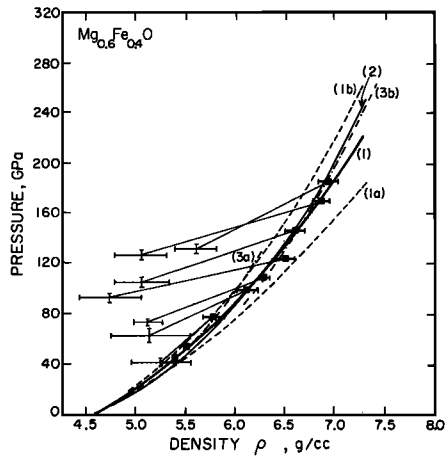

Fig. 2 Porosity-corrected Hugoniot data for $Mg_{0.6}Fe_{0.4}O$, with release data, in pressure-density space. Curve 1 is a two-parameter (K_0 and K_0') least squares fit of a third order Eulerian Hugoniot to the data. The fitted Hugoniot is calculated via a thermal correction from the principal isentrope, so that the modulus values are isentropic. Curves 1(a) and 1(b) are bounds to Curve 1, calculated by using extremal values of K_0 and K_0' within their error ranges. Curve 2 is a fit to the data with K_0 constrained to its ultrasonic value of 161.5 GPa. Curves 3(a) and 3(b) are respectively low and high pressure phase third order Eulerian Hugoniots under the hypothesis of a phase transition. They are chosen to demonstrate the maximum magnitude of phase transition that could be consistent with the data.

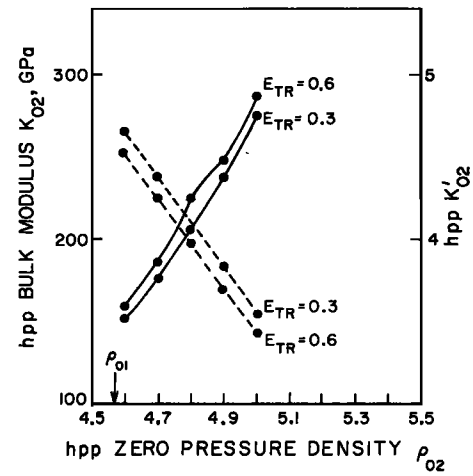

Fig. 4 Best fit K_{02} (rising curves) and K_{02}' (falling curves) for a hypothetical high pressure phase for various choices of ρ_{02} (the hpp initial density). The assumed transition energies are 0.6 MJ/kg for one set of curves and 0.3 MJ/kg for the other.

We note first that 120 GPa is a likely transition pressure for this composition, assuming ideal solid solution behavior and a small volume transition in MgO above 200 GPa. This can be seen by examining Fig. 3, which presents some examples of pressure-composition curves calculated under the assumption of ideality, according to the method described by Meijering and Rooymans (1958). Of course, these are equilibrium diagrams, and one might not expect the implied compositional segregation to occur under shock as under static conditions, but such diagrams can still give us a clue about expected transition pressures.

We consider the hypothesis that there is a phase transition at ~ 120 GPa, and that the upper four points represent data for the high pressure phase (hpp). In order to calculate the third order Eulerian fit to the hpp, one must consider at least four

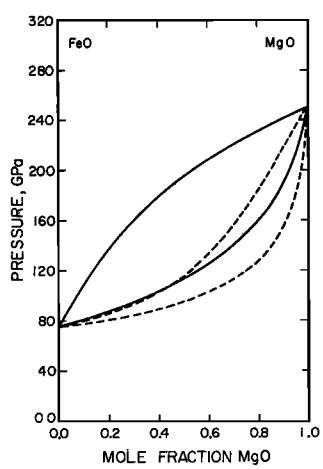

Fig. 3 Pressure-Composition phase diagram calculations for the solid solution MgO-FeO assuming ideal behavior. These curves are for a temperature of 3000 °C, and transition pressures of 75 GPa and 250 GPa for FeO and MgO respectively. The solid lines assume a 4% density change for the transitions in both endmembers; the dotted lines are for density changes of 4% for FeO and 1% for MgO.

parameters: K_{02}, K_{02}', E_{TR} (the transition energy), and ρ_{02} (the hpp initial crystal density). This is the case provided that a guess is made for $\gamma(\rho)$; we use $\gamma_0 = 1.5$, and $\rho\gamma$ = constant. Conceivably, a radically different $\gamma(\rho)$ for the hpp could affect the porosity correction in the hpp region enough to increase the visible density change associated with the hypothetical transition; such effects, however, are generally small, and in any case $\gamma(\rho)$ is unknown. Since even a two-parameter fit for K_{02} and K_{02}' is not well constrained by four data points, we make several choices for ρ_{02} and for a given choice estimate E_{TR} from the product $P_{TR}\Delta V_{TR}$, where we neglect an entropy term likely to be small (McQueen et al, 1963). To estimate effectively the volume change ΔV_{TR} of the transition, we need some knowledge of the hpp Hugoniot, so some iteration is involved. If we fit a curve to the low pressure phase (lpp) assuming that this is represented by the lowest 4 data, we find that it essentially coincides with Curve 1, and does not suggest any phase transition. If we make the fit to the lpp including only the lowest 3 points, we obtain Curve 3(a). We do not consider this a likely representation, but choose it to maximise the magnitude of the hypothetical phase transition and obtain an upper bound. The maximum E_{TR} we estimate for the transition is 0.6 MJ/kg, corresponding to an upper bound density increase of roughly 3%. Fig. 4 shows the best fit K_{02} and K_{02}' for a variety of choices of ρ_{02}. The various curves that can be drawn for the hpp using the parameters in Fig. 4 are essentially the same above the transition, and well represented by Curve 3(b); they can differ considerably, however, at lower pressures. The inferred zero pressure density increase for our transition differs depending on the assumed properties of the hpp. As can be seen from Fig. 4, high increases are inferred when K_{02} is high and K_{02}' is low.

As we have stated, we do not believe that our data provide sufficient evidence for a phase transition, although we cannot rule one out. The arguments we have made above suggest that if a transition indeed occurs, it is of relatively small volume change compared to the transition in wustite. We do not believe that phase transitions in (Mg,Fe)O are of direct importance to the lower mantle. Of course, even a relatively small volume transition could still explain some of the features of D'', depending on changes in the elastic moduli. If we are willing to accept the hypothesis of a phase transition in our data, we must recognize that there could be

substantial changes in K_0, despite the probably small volume change (see Fig. 4). Also possibly important (Jeanloz, personal communication) are changes in the shear modulus, particularly if the transition involves a coordination change. The most accurate statement of our position is not that we disbelieve (Mg,Fe)O to be responsible for the effects in D'' because the volume change in its phase transition is small-- it is that we feel that our data do not offer sufficient evidence of a transition at all. Whatever the nature of the phase transition in FeO, we are faced with the same two alternatives discussed by Vassiliou and Ahrens (1981): (1) Phase changes may be occurring all across the solid solution, isostructural to the transition in FeO, but with a volume change that declines significantly towards the Mg-rich end; and (2) The transition in FeO is effectively localised to the Fe-rich end, with no transitions at all near the Mg-rich end, perhaps because it is an effect of non-stoichiometry.

4. Summary of Conclusions

(1.) When fit by a third order Eulerian Hugoniot with K_0 equal to its ultrasonic value of 161.5 GPa (Bonczar and Graham, 1981), our data for the magnesiowustite $Mg_{0.6}Fe_{0.4}O$ yield a K_0' of 4.37 +/- 0.37, significantly lower than the ultrasonic value of 6.18. The isothermal compression data of Rosenhauer et al (1976) are more compatible with our value of K_0' than with the ultrasonic one.

(2) We do not believe that our data offer sufficient evidence of a phase transition in $Mg_{0.6}Fe_{0.4}O$, although we cannot rule one out. A phase transition at 120 GPa with a 3% density increase is marginally consistent with the data; smaller transitions are more consistent. Although it is possible that the wustite phase change is a first order transition occurring isostructurally across the MgO-FeO solid solution with a decreasing volume change towards the Mg end, our data could also suggest that it is a more complex phenomenon, perhaps arising from nonstoichiometry, localised to the iron-rich end.

(3) Because there is not sufficient evidence for a phase transition in our magnesiowustite, we do not believe that transformations in lower-mantle (Mg,Fe)O should be invoked as an explanation for the seismic anomalies of the D'' region (e.g., as in Jeanloz and Ahrens, 1980).

Acknowledgements. We gratefully acknowledge the experimental expertise of E. Gelle and M. Long, who operate the shock-wave facility in the Lindhurst Laboratory of Experimental Geophysics at Caltech. Discussions with Raymond Jeanloz, Don Anderson, and Glen Waychunas were very helpful. We are indebted to Earl Graham of the Pennsylvania State University for providing us with our samples of magnesiowustite. This research was supported by the Earth Sciences Section, National Science Foundation, grant # EAR79-26384.

(Contribution # 3700, Division of Geological and Planetary Sciences, California Institute of Technology)

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(Received September 11, 1981;
revised November 2, 1981;
accepted December 2, 1981.)