

## EQUATIONS OF STATE OF OLIVINE-TRANSFORMED SPINELS

D.H. CHUNG

*Department of Earth and Planetary Sciences,  
Massachusetts Institute of Technology,  
Cambridge, Mass. 02139, USA*

Received 4 January 1971

Revised version received 23 January 1972

Based on our recent data on the elasticity of olivine in the forsterite-fayalite series, Birch's law for the velocity-density-mean atomic weight relation is used to construct the equations of state of spinels in the  $Mg_2SiO_4-Fe_2SiO_4$  system. The equations of state of these olivine-transformed spinels are first presented and then discussed in relation to the equations of state of the same compositions in the olivine structure. Effects of the iron/magnesium ratios in these mineral systems on the solid equations of state are discussed. We conclude that (1) Birch's law is a useful scheme by which we can deduce equation-of-state parameters of the yet unmeasured olivine-transformed spinels; (2) the olivine-transformed spinels are less compressible than olivines at all pressures; (3) the  $\beta$ - $Mg_2SiO_4$  (spinel) is more compressible than the  $Fe_2SiO_4$ -spinel, although in the olivine structure fayalite was seen to be more compressible than forsterite; and (4) the incompressibility values for the olivine-transformed spinels are in the neighborhood of 2 Mb and their first pressure derivatives range from 4 to 5 as the iron/magnesium ratio in the lattice increases.

## 1. Introduction

The equations of state of solid phases in the  $Mg_2SiO_4-Fe_2SiO_4$  system are of special interest in the study of the physics and chemistry of the earth's mantle. The transition region at a depth of about 350 km in the earth is characterized by an abrupt increase in seismic velocity. This seismic observation has been attributed to pressure-induced changes in the crystal structure of the mantle materials. Laboratory petrological studies at high pressures and high temperatures (see, for example, Ringwood [1] for a review) have shown that olivine, a major component of the mantle, transforms to a spinel type structure with a density increase of about 10%. D.L. Anderson [2] attributed the seismic velocity jump observed at about 400 km in the earth to this olivine-spinel phase change. A study of the equations of state of solid phases in these mineral systems is then essential in geophysics for a better understanding of the mechanical and thermal state of the mantle. The equations of state of olivines as functions of iron/magnesium ratios

have been studied in an earlier paper [3]; the equations of state of olivine-transformed spinels in the  $(Mg_xFe_{1-x})_2SiO_4$  series are presented in this communication as part of our continuing investigations.

Laboratory determination of sound velocities in the olivine-transformed spinels is not easy. The difficulty in the experiment is two fold: (1) one has to produce the olivine-transformed spinels in the sufficient quantity under high-pressure and high-temperature conditions and (2) one must be able to sinter the material in a dense form without converting it back to olivine (or, one must be able to grow the olivine-transformed spinel single-crystals large enough to make acoustic measurements on them).

The first part of this paper presents the elastic constants and the equation-of-state parameters of olivine-transformed spinels, deduced from the application of Birch's law, followed by a comparison of these equations of state with experimental compression data. Effects of iron/magnesium ratios on the equations of state for these mineral systems are then illustrated.

## 2. Birch's law and equation-of-state parameters

Birch [4, 5] in 1961 observed that the velocity of compressional waves  $V_p$  in minerals and rocks depends essentially on density in a linear fashion for substances with similar mean atomic weight. He made this important observation on the basis of his systematic investigation [5, 6] of the behavior of compressional wave velocities in minerals and rocks at high pressure. Birch [4] then concluded that the velocity  $V_p$  in isotropic aggregates of oxides and silicates is mainly a function of density and mean atomic weight and that the variation of density for substances with the same mean atomic weight reflects structural and compositional differences. This is known today as Birch's law for the velocity-density-mean atomic weight relation. McQueen et al. [7] observed for similar materials that the bulk sound velocity  $V_\phi$ , frequently called the "hydrodynamical velocity", is proportional to density. Wang [8] also observed the linear variation of the bulk sound velocity with density in compressed periclase. Based on velocity measurements of shear waves  $V_s$  in minerals and rocks, Simmons [9] observed that the shear wave velocity also is a linear function of density, although a few exceptions to the above were noted by Simmons [9]. These

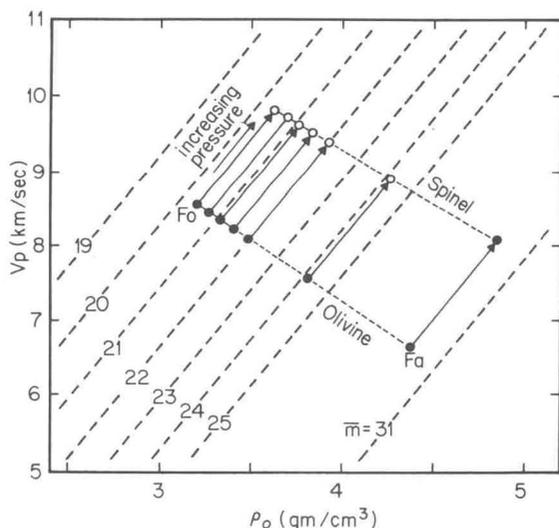


Fig. 1. Velocity of compressional waves-density-mean atomic weight relation for olivine and the olivine-transformed spinels in the  $(Mg_xFe_{1-x})_2SiO_4$  system. The olivine data are from refs. [3, 10] and the olivine-transformed spinel data are estimated values.

observations essentially support Birch's law, and they have important implications in geophysics since they enable one to estimate velocities of elastic waves in solid phases that are as yet unmeasured.

The velocities of compressional and bulk waves in olivines with different  $Fe/(Mg + Fe)$  ratios are plotted in figs. 1 and 2, respectively, as a function of density. The data on these velocities are from recent work of this author, and they are based on a systematic measurement of the velocity of both compressional and shear waves in synthetic olivine polycrystals [3, 10]. Under pressure, the density of an olivine with a specific  $(Fe/Mg)$  ratio would increase through a gradual decrease in mean atomic volume, while the velocity of elastic waves will increase in the manner illustrated in fig. 3. The path indicated by the dashed line would be the actual velocity-density trajectory as the olivine is compressed. Olivine transforms into a spinel structure at high pressure; this phase change is accompanied by a density increase of 10 to 12%. Knowing the end-point density of the olivine-transformed spinel, we can estimate its velocity in the manner illustrated in fig. 3. Thus, as noted before [3, 10], the velocity

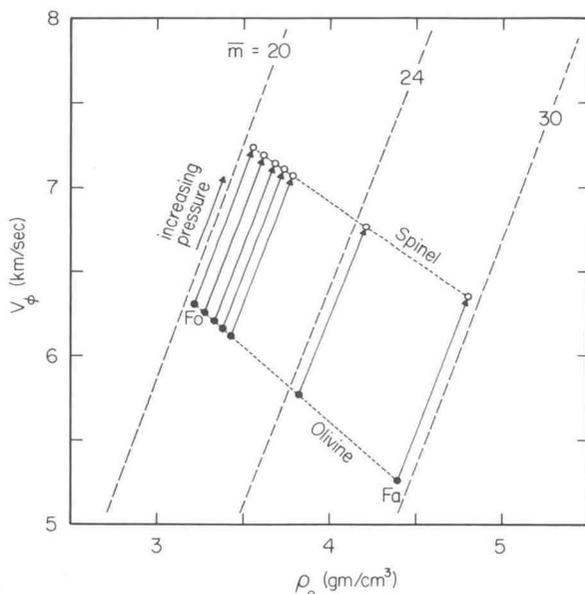


Fig. 2. Bulk sound velocity-density-mean atomic weight relation for olivines and the olivine-transformed spinels in the  $(Mg_xFe_{1-x})_2SiO_4$  system. The olivine data are from [3, 10] and the olivine-transformed spinel data are estimated values.

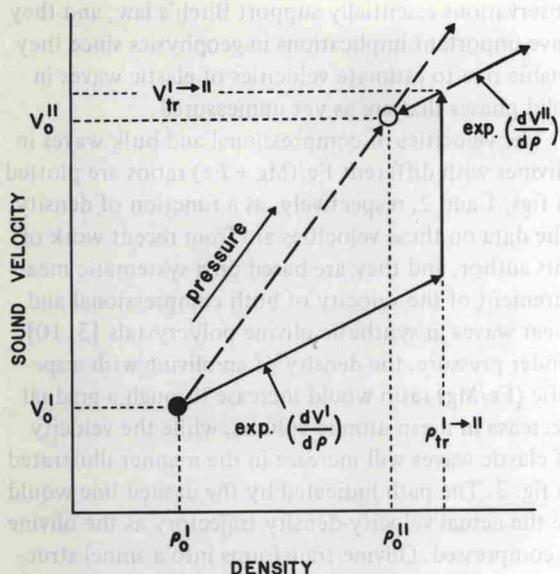


Fig. 3. The density-velocity relation for a solid undergoing the first-order phase change.

after interpolation to zero pressure would be represented by an intercept of two lines drawn from density and mean atomic weight as shown in figs. 1 and 2. In table 1 these estimated velocities for the olivine-transformed spinels in the  $Mg_2SiO_4$ - $Fe_2SiO_4$  system are listed. In their recent publication, Mizutani et al. [11] reported that they have successfully prepared a fayalite-transformed spinel sample and measured the compressional velocity of  $8.0 (\pm 0.1)$  km/sec at ambient conditions. This value is about 21% greater than the compressional velocity measured in fayalite samples as noted in ref. [10]. The compressional velocity of 8.0 km/sec [11] is in remarkable agreement with 8.05 km/sec, a  $V_p$  value found by the intercept of the two lines drawn for the density and the mean atomic weight [3, 10]; thus, again, Birch's law is seen to be confirmed.

The bulk modulus also changes with phase change. Since the adiabatic bulk modulus  $K_s$  is related to density  $\rho$  and the bulk sound velocity  $V_\phi$  by

$$K_s = \rho V_\phi^2 \quad (1)$$

$K_s$  can be evaluated. The  $K_s$  values thus found for the olivine-transformed spinels are listed in the 8th column of table 1 and compared in fig. 4 with the respec-

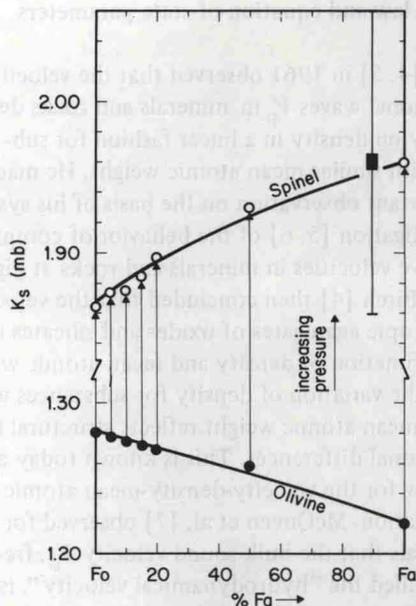


Fig. 4. Bulk modulus of olivines and the olivine-transformed spinels in the  $(Mg_xFe_{1-x})_2SiO_4$  system. The olivine data points are from [3, 10] and the olivine-transformed spinel data points are estimated values. The datum point ( $\blacksquare$ ) is from isothermal compression data in ref. [12] found by a curve-fitting procedure using the Birch equation of state with the assumption that  $(\partial K/\partial p) = 4$ .

tive  $K_s$  values in the olivine structure. Values of the bulk modulus show about a 45% increase for  $\beta$ - $Mg_2SiO_4$  (spinel) and 61% increase for the  $Fe_2SiO_4$ -spinel from their respective bulk modulus values in the olivine phase.

These estimated  $K_s$  values may be compared with literature data on isothermal bulk modulus values reported by Mao et al. [12], after appropriate correction for adiabatic to isothermal modulus is made. Mao et al. [12] presented values of the isothermal bulk modulus  $K$  (found by a curve-fitting procedure using the Birch equation of state with the assumption that  $(\partial K/\partial p)_T = 4$ ) for three olivine-transformed spinels from their measurements of volume change with pressure. Their results [12] are  $2.12 (\pm 0.10)$ ,  $1.96 (\pm 0.10)$ , and  $2.08 (\pm 0.10)$  Mb for the isothermal bulk modulus of  $Fe_2SiO_4$ -spinel,  $(Mg_{0.1}Fe_{0.9})_2SiO_4$ -spinel, and  $(Mg_{0.2}Fe_{0.8})_2SiO_4$ -spinel, respectively. These values of  $K$  reported by Mao et al. [12] compare favorably with 1.96, 1.95, and 1.94 Mb, respectively, calculated from eq. (1) for spinels of the same compositions.

Table 1  
Elastic properties of olivine and olivine-transformed spinels in the  $Mg_2SiO_4-Fe_2SiO_4$  system \*.

Mg/(Mg+Fe) ratio, mole %	Phase	$\bar{m}$	$\rho$ (g/cm <sup>3</sup> )	$V_p$	$V_s$ (km/sec)	$V_s$	$K_s$ (Mb)	$\left(\frac{\partial K_s}{\partial \rho}\right)$	Remarks
100	Olivine	20.1	3.217	8.534	4.977	6.309	1.281	5.04	Experimental
	Spinel	20.1	3.556	9.66	5.54	7.24	1.86	4.4	Estimated
95	Olivine	20.6	3.273	8.422	4.892	6.245	1.277	5.08	Experimental
	Spinel	20.6	3.620	9.57	5.48	7.18	1.87	4.4	Estimated
90	Olivine	21.0	3.330	8.317	4.815	6.189	1.274	5.13	Experimental
	Spinel	21.0	3.683	9.49	5.42	7.13	1.87	4.5	Estimated
85	Olivine	21.5	3.386	8.216	4.739	6.132	1.272	5.13	Experimental
	Spinel	21.5	3.750	9.41	5.36	7.10	1.88	4.5	Estimated
80	Olivine	21.9	3.440	8.116	4.663	6.075	1.269	5.23	Experimental
	Spinel	21.9	3.815	9.33	5.29	7.05	1.89	4.6	Estimated
50	Olivine	24.6	3.800	7.534	4.213	5.753	1.258	5.44	Experimental
	Spinel	24.6	4.209	8.85	4.92	6.78	1.93	4.8	Estimated
0	Olivine	29.1	4.393	6.637	3.494	5.273	1.220	5.92	Experimental
	Spinel	29.1	4.849	8.05	4.28	6.35	1.96	5.1	Estimated
			$\pm 0.2\%$	$\pm 0.5\%$	$\pm 0.5\%$	$\pm 0.8\%$	$\pm 1.8\%$	$\pm 5.0\%$	Expected error

\* Data from ref. [3].

Birch's law for the bulk sound velocity-density-mean atomic weight relation is

$$V_{\phi} = a + b\rho \quad (2)$$

where the constants  $a$  and  $b$  can be obtained from a least squares fit of experimental values of  $V_{\phi}$  obtained from substances of similar mean atomic weight (or from substances of the same mean atomic weight, as was done by Wang [8]). In terms of Birch's law, Chung [13] has shown that

$$\left(\frac{\partial K_s}{\partial p}\right)_{s,\bar{m}} = 1 + \frac{2b\rho}{V_{\phi}} + \frac{c}{K_s} \quad (3)$$

where  $K_s$  is in megabars and  $V_{\phi}$  is in kilometers per second. Using eq. (3), values of  $(\partial K_s/\partial p)$  for the olivine-transformed spinels were calculated from  $\rho$ ,  $V_{\phi}$ , and  $K_s$  in table 1; in table 2, these calculated results are then compared with earlier estimates made by this author. The agreement between these two sets is satisfactory.

Although the chemistry of spinels in the (Mg,Fe)  $\text{Al}_2\text{O}_4$  compositions differs from that of the (Mg,Fe) $_2$   $\text{SiO}_4$ -spinel, their elastic properties are probably identical.\* Support for the present estimates of equation-of-state parameters for the olivine-transformed

\* From the structural point of view, the spinels in the (Mg, Fe)  $\text{Al}_2\text{O}_4$  system differ in two ways from those of the (Mg, Fe)  $_2$   $\text{SiO}_4$  composition. In the former case, there are 8 (Mg, Fe)  $\text{Al}_2\text{O}_4$  units per unit cell, wherein the divalent cations are in the fourfold coordination and two trivalent aluminum ions are in the sixfold coordination. In the latter case, there are 8 (Mg, Fe)  $_2$   $\text{SiO}_4$  units per unit cell; the divalent cations, which are twice as numerous as the tetravalent silicon in a given unit cell, are in the fourfold coordination and the silicon ion in the sixfold coordination. In both cases, however, the structure consists of a cubic closely-packed array of oxygen ions with the sixfold coordinated cations occupying the octahedral interstices and the divalent cations the tetrahedral interstices. Ionic sizes of these cations in the octahedral sites do not differ much, i.e., according to Pauling [14]  $\text{Al}^{3+}$  has the ionic radius of 0.50Å and  $\text{Si}^{4+}$  has 0.41Å. One would expect that, for the same (Fe/Mg) ratio in the tetrahedral sites in these two spinel compositions, the elastic properties like the bulk modules and its rate of change with pressure would not differ very much from each other. However, because there are twice the number of iron atoms in the (mg,Fe)  $_2$   $\text{SiO}_4$  composition as compared with the (Mg, Fe)  $\text{Al}_2\text{O}_4$  spinels, the greater effect of an iron substitution for magnesium on the elastic properties would be expected for the (Mg,Fe) $_2$   $\text{SiO}_4$  composition than for the  $\text{Al}_2\text{O}_4$  spinels.

spinel then comes from recent ultrasonic measurements of  $(\partial K_s/\partial p)$  for spinels in the (Mg,Fe)  $\text{Al}_2\text{O}_4$  system. The elastic constants of the stoichiometric  $\text{MgAl}_2\text{O}_4$  spinel were first studied by Chung et al. [15] with hot-pressed polycrystalline samples. Lewis [16] and more recently O'Connell and Graham [17] studied the single-crystal elastic properties of this spinel; their results at ambient conditions are found to be in good agreement with the results from polycrystalline work. Schreiber [18] measured a  $(\partial K_s/\partial p)_T$  value of 4.18 for a spinel with the Mg(2.6)  $\text{Al}_2\text{O}_4$  composition. Chung [32], working with polycrystalline stoichiometric  $\text{MgAl}_2\text{O}_4$  spinel, determined a  $(\partial K_s/\partial p)_T$  value of 4.3 ( $\pm 0.25$ ). Using spinel of the same composition, but working with single crystals, O'Connell and Graham [17] found the value of 3.76. O'Connell and Graham [17] also measured  $(\partial K_s/\partial p)_T = 3.76$  for the same specimen of Mg(2.6)  $\text{Al}_2\text{O}_4$  spinel that Schreiber [18] used in his original work; thus the apparent disagreement is noted for the work of refs. [17] and [18]. (The apparent difference in the  $(\partial K_s/\partial p)_T$  value measured on the same sample, but different investigators, seems to represent the present state-of-the-art in the attempt to characterize this important equation-of-state parameter of mantle minerals). In their recent paper, Wang and Simmons [19] reported a  $(\partial K_s/\partial p)$  value of 4.9 ( $\pm 0.25$ ) for a pleonaste-spinel of the "(Mg<sub>0.75</sub>Fe<sub>0.36</sub>)  $\text{Al}_{1.9}\text{O}_4$  composition". For comparison with the elastic parameters estimated for spinels in the (Mg<sub>x</sub>Fe<sub>1-x</sub>)  $_2$   $\text{SiO}_4$  system, the density and other parameters of various spinels in the (Mg,Fe)  $\text{Al}_2\text{O}_4$  compositions are listed in table 3. As is clearly shown in table 2 and 3, the elastic properties of these spinel compositions are similar; values of  $K_s$  are in the neighborhood of 2 Mb and for  $(\partial K_s/\partial p)$  values are about 4 to 5. Thus, in the absence of experimental measurement, the equation-of-state parameters of the (Mg<sub>x</sub>Fe<sub>1-x</sub>)  $_2$   $\text{SiO}_4$ -spinel estimated in this report provide a basis for specifying the desired equations of state of these olivine-transformed spinels in the  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  system.

Table 2  
Estimated values of  $K_S$  and  $(\partial K_S/\partial p)$  for spinels in the  $Mg_2SiO_4-Fe_2SiO_4$  system.

Mg/(Mg+Fe) ratio, mole %	$\rho$ ( $g/cm^3$ )	$K_S$ (Mb)	from eq. (3) $(\partial K_S/\partial p)$	from table 1 $(\partial K_S/\partial p)$
100	3.556	1.86	4.1	4.4
95	3.620	1.87	4.2	4.4
90	3.683	1.87	4.2	4.5
85	3.750	1.88	4.3	4.5
80	3.815	1.89	4.4	4.6
50	4.209	1.93	4.8	4.8
0	4.849	1.96	5.5	5.1

Table 3  
Elastic properties and equation-of-state parameters of spinels in the  $(Mg,Fe) Al_2O_4$  system.

Composition	$\rho$ ( $g/cm^3$ )	$V_p$ (km/sec)	$V_s$ (km/sec)	$\mu$ (Mb)	$K_S$ (Mb)	$\left(\frac{\partial K_S}{\partial p}\right)_T$	Ref.
MgAl <sub>2</sub> O <sub>4</sub> (p) *	3.581	9.761	5.492	1.080	1.972	4.30( $\pm$ 0.25)	[15]
MgAl <sub>2</sub> O <sub>4</sub> (s)	3.581	9.764	5.492	1.080	1.974	3.76( $\pm$ 0.04)	[17]
MgAl <sub>2</sub> O <sub>4</sub> (s)	3.581	9.712	5.465	1.072	1.950	—	[16]
Mg(2.6) Al <sub>2</sub> O <sub>4</sub> (s)	3.619	9.914	5.642	1.154	2.020	4.18( $\pm$ 0.09) ***	[18]
Mg(2.6) Al <sub>2</sub> O <sub>4</sub> (s)	3.619	9.914	5.642	1.154	2.020	3.76( $\pm$ 0.04) ***	[17]
Mg(3.5) Al <sub>2</sub> O <sub>4</sub> (s)	3.630	9.928	5.660	1.164	2.026	—	[33]
Pleonaste ** (s)	3.826	9.265	5.043	0.973	1.987	4.90( $\pm$ 0.25)	[19]

\* (p) stands for polycrystalline samples and (s) stands for single-crystal samples.

\*\* This pleonaste has a "[0.75]Mg[0.36]Fe]Al<sub>1.90</sub>O<sub>4</sub> composition" [19].

\*\*\* This apparent difference in the  $(\partial K_S/\partial p)$  values measured on the same sample, but by different investigators, seems to indicate the present inaccuracies in the attempt to characterize this important equation-of-state parameter of mantle minerals.

### 3. Equations of state

The forms of solid equations of state most often used in geophysics are those of Murnaghan and Birch. The Murnaghan equation of state [20], derived from the theory of finite strain, is an approximation in which the instantaneous bulk modulus is assumed to be a linear function of pressure. O.L. Anderson [21, 22], following Ryabinin [23], demonstrated with fifteen substances an applicability of the Murnaghan equation for predicting the compression curve of a solid; however, a perusal of the theory of the Murnaghan equation of state indicates that the Murnaghan equation should not be used for a solid in a pressure range above 0.5K. As stated by Chung et al. [24], use of the

Murnaghan equation of state would lead to overestimates of the density and the seismic parameter  $\phi$  at high pressures. The reasoning here is associated not only with the Murnaghan assumption of a linear variation of the bulk modulus with pressure but also with an inadequacy of the functional form of the equation itself. In his review, Macdonald [25, 26] presented several other limitations for the use of the Murnaghan equation of state at high pressures; he concluded from thermodynamics that the Murnaghan equation yields a finite negative pressure at which the density approached a finite value which is an unacceptable result. Therefore, we use the Birch equation in our discussion of equations of state for the olivine-transformed spinels.

While the Murnaghan equation of state was found by integrating a Taylor expansion of the bulk modulus in pressure, the Birch equation of state is based on the Taylor expansion of the strain energy with respect to the Eulerian strain components. Thus, the Birch equation of state is a phenomenological equation based on the rapidly converging Taylor expansion of the interatomic potential; the equation was derived from the finite strain theory of Murnaghan with the cubic and quadratic terms of the strain retained in the expression for Helmholtz free energy [27, 28]:

$$p = (3K_0/2)(y^7 - y^5) [1 + \frac{3}{4}(m-4)(y^2 - 1)] \quad (4)$$

where  $y = (V_0/V)^{1/3} = (\rho/\rho_0)^{1/3}$ .  $K_0$  and  $m$  are material parameters corresponding to the isothermal bulk modulus and its first pressure derivative evaluated at zero pressure. (If eq. (4) is used in an adiabatic form,  $K_0$  and  $m$  are respectively the adiabatic bulk modulus and

the adiabatic pressure derivative of the adiabatic bulk modulus).

Therefore, we propose the following equations of state for the olivine-transformed spinels in the  $(Mg_xFe_{1-x})_2SiO_4$  system:

$$\text{For } \beta\text{-Mg}_2\text{SiO}_4\text{-spinel : } p(\text{in Mb}) \\ = 2.79 (y^7 - y^5) [1.3(y^2 - 1)]$$

$$\text{For } \beta\text{-(Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4 : p(\text{in Mb}) \\ = 2.81 (y^7 - y^5) [1.4(y^2 - 1)]$$

$$\text{For } (\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4 : p(\text{in Mb}) \\ = 2.84 (y^7 - y^5) [1.5(y^2 - 1)] \quad (5)$$

$$\text{For } (\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4 : p(\text{in Mb}) \\ = 2.89 (y^7 - y^5) [1.6(y^2 - 1)]$$

$$\text{For } \text{Fe}_2\text{SiO}_4 \text{ (spinel) : } p(\text{in Mb}) \\ = 2.94 (y^7 - y^5) [1.8(y^2 - 1)]$$

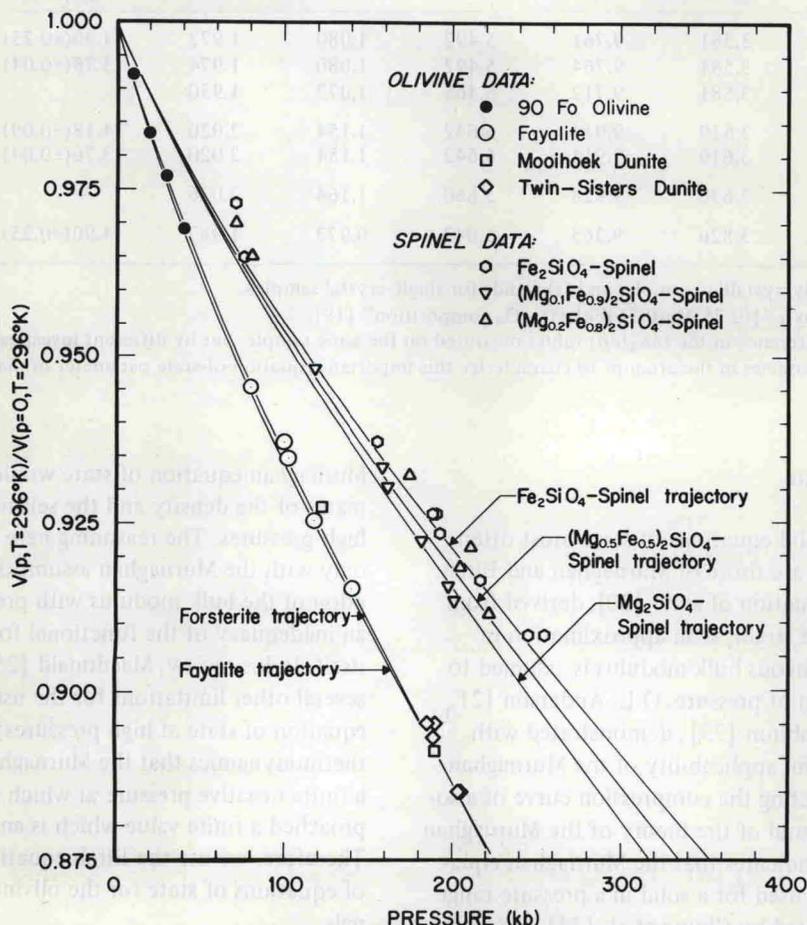


Fig. 5. Volume-pressure trajectories for olivines and the olivine-transformed spinels; comparison with isothermal compression data due to ref. [12]. The solid lines are from the present work, and they are independent of the compression data points.

The volume-pressure trajectories inferred from the Birch equation of state are shown in fig. 5 for olivines and the olivine-transformed spinels in the  $\text{Mg}_2\text{SiO}_4$ – $\text{Fe}_2\text{SiO}_4$  series. The equations of state of olivines in the forsterite-fayalite series have been presented earlier [3], and they are merely reproduced here to compare them with those of the olivine-transformed spinels. The points entered in fig. 5 are isothermal compression data of a peridot-olivine, due to Bridgman [29], and of a fayalite-olivine due to recent work of Takahashi [30] \*. The shock-compression data of McQueen et al. [31] for natural dunites are also compared with the volume-pressure trajectories for olivine. For the olivine-transformed spinels in the  $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$  system, the only compression data, due to Mao et al. [12], are compared with the volume-pressure trajectories derived from eq. (5). It is apparent from fig. 5 that, although the present comparison is made for a pressure range of about 15% of the bulk modulus, there is a strong evidence of agreement between the experimental compression data and the present equations of state of the olivine-transformed spinels. This agreement in turn may serve as supporting evidence for the idea presented in this communication.

In addition, there is an important observation to be made from fig. 5. Shown here are the effects of iron/magnesium ratios on the compression curves of olivines and the olivine-transformed spinels in the  $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$  system. Effects of an iron substitution for magnesium in these crystal lattices on the compression curve are such that the  $\text{Fe}_2\text{SiO}_4$ -spinel is less compressible than the  $\beta$ - $\text{Mg}_2\text{SiO}_4$  (spinel) at all pressures, whereas in the olivine structure we have seen [3] that forsterite is less compressible than fayalite. It may be of interest to note that, if the compression trajectories for forsterite and fayalite are extended to pressures above their olivine-spinel phase transformation pressures, these two compression trajectories cross over at a pressure of about 180 ( $\pm 20$ )

\* It may be noted that Takahashi found  $K = 1.35 (\pm 0.15)$  Mb by a curve-fitting procedure using the Murnaghan equation of state with the assumption that  $(\partial K/\partial p) = 4.5$  for fayalite. As is shown in ref. [3], the  $(\partial K/\partial p)$  measured on fayalite samples is  $5.97 (\pm 0.32)$ ; using this value of  $(\partial K/\partial p)$  in the Murnaghan and Birch equations of state results in a  $K$  value of  $1.2 (\pm 0.08)$  Mb. This new value of the isothermal bulk modulus  $K$  is in good agreement with  $1.211 (\pm 0.024)$  Mb reported in ref. [10].

kb (corresponding to a volume ratio of  $(V/V_0) = 0.9$ ). Above this pressure, fayalite is less compressible than forsterite; this extended observation is consistent with the compression curves of the olivine-transformed spinels presented in this paper.

### Acknowledgment

Financial support received from the National Science Foundation under Grant GA-11091 is gratefully acknowledged.

### References

- [1] A.E. Ringwood, Phase transformations in the mantle, *Earth Planet. Sci. Letters* 5 (1969) 401.
- [2] D.L. Anderson, Phase changes in the upper mantle, *Science* 157 (1967) 1165.
- [3] D.H. Chung, Elasticity and equations of state of olivines in the  $\text{Mg}_2\text{SiO}_4$ – $\text{Fe}_2\text{SiO}_4$  system, *Geophys. J.* 25 (1971). 571
- [4] F. Birch, Composition of the earth's mantle, *Geophys. J.* 4 (1961) 295.
- [5] F. Birch, The velocity of compressional waves in rocks to 10 kilobars, Part 2, *J. Geophys. Res.* 66 (1961) 2199.
- [6] F. Birch, The velocity of compressional waves in rocks to 10 kilobars, Part 1, *J. Geophys. Res.* 65 (1960) 1083.
- [7] R.G. McQueen, J.N. Fritz and S.P. Marsh, On the composition of the Earth's interior, *J. Geophys. Res.* 69 (1964) 2947.
- [8] C.Y. Wang, Equation of state of periclase and some of its geophysical implications, *J. Geophys. Res.* 74 (1969) 1451.
- [9] G. Simmons, Velocity of shear waves in rocks to 10 kilobars, *J. Geophys. Res.* 69 (1964) 1123.
- [10] D.H. Chung, Effects of iron/magnesium ratio on P- and S-wave velocities in olivine, *J. Geophys. Res.* 75 (1970) 7353.
- [11] H. Muzitani, Y. Hamano, Y. Ida and S. Akimoto, Compressional wave velocities in fayalite,  $\text{Fe}_2\text{SiO}_4$ -spinel, and coesite, *J. Geophys. Res.* 75 (1970) 2741.
- [12] H. Mao, T. Takahashi, W.A. Bassett, J.S. Weaver and S. Akimoto, Effect of pressure and temperature on the molar volumes of wustite and of three  $(\text{Fe,Mg})_2\text{SiO}_4$ -spinel solid solutions, *J. Geophys. Res.* 74 (1969) 1061.
- [13] D.H. Chung, On the solid equations of state of high-pressure polymorphs, to be published.
- [14] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948).
- [15] D.H. Chung, P.O. Benson and W.B. Crandall, Elastic properties of magnesium-aluminate spinels, *Tech. Rept.* 6 (1963), Army Research Office Contract no. DA-31-124-ARO (D-23).

- [16] M.F. Lewis, Elastic constants of magnesium aluminate spinel, *J. Acoust. Soc. Am.* 40 (1966) 729.
- [17] R.J. O'Connell and E.K. Graham, Equation of state of stoichiometric spinel to 10 kbar and 800°K. *Trans. Am. Geophys. Union* 52 (1971) 359.
- [18] E. Schreiber, Elastic moduli of single crystal spinel at 25°C and to 2 kbar, *J. Appl. Phys.* 38 (1967) 2508.
- [19] H. Wang and G. Simmons, The elastic constants of an iron-bearing spinel, *Trans. Am. Geophys. Union* 52 (1971) 358. [It is noted that some of the values presented in the paper abstract have been revised in personal communications. The data cited in table 4 of this paper are correct, according to H. Wang.]
- [20] F.D. Murnaghan, *Finite Deformation of an Elastic Solid* (Wiley, New York, 1951) 73.
- [21] O.L. Anderson, Two methods for estimating compression and sound velocity at very high pressures, *Proc. Nat. Acad. Sci.* 54 (1965) 667.
- [22] O.L. Anderson, The use of ultrasonic measurements under modest pressure to estimate compression at high pressure, *J. Phys. Chem. Solids* 27 (1966) 547.
- [23] I.N. Ryabinin, Volume compressibility of elements at ultrahigh pressure, *Fiz. Metal. Metalloved.* 2 (1956) 225.
- [24] D.H. Chung, H. Wang, and G. Simmons, On the calculation of the seismic parameter at high pressure and high temperatures, *J. Geophys. Res.* 75 (1970) 5113.
- [25] J.R. Macdonald, Some simple isothermal equations of state, *Rev. Mod. Phys.* 38 (1966) 669.
- [26] J.R. Macdonald, Review of some experimental and analytical equations of state, *Rev. Mod. Phys.* 41 (1969) 316.
- [27] F. Birch, Elasticity and constitution of the Earth's interior, *J. Geophys. Res.* 57 (1952) 227.
- [28] F. Birch, Finite elastic strain of cubic crystals, *Phys. Rev.* 71 (1947) 809.
- [29] P.W. Bridgman, The compression of 39 substances to 100,000 kg/cm<sup>2</sup>, *Proc. Am. Acad. Arts Sci.* 76 (1948) 55.
- [30] T. Takahashi, Isothermal compression of fayalite at room temperature, *Trans. Am. Geophys. Union* 51 (1970) 827.
- [31] R.G. McQueen, S.P. March and J.N. Fritz, Hugoniot equation of state of 12 rocks, *J. Geophys. Res.* 72 (1967) 4999.
- [32] D.H. Chung, Equations of state of magnesium-aluminate spinels, to be published.
- [33] R.K. Verma, Elasticity of some high-density crystals, *J. Geophys. Res.* 65 (1960) 757.