

## Effect of Pressure and Temperature on the Molar Volumes of Wüstite and of Three $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ Spinel Solid Solutions

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The effect of pressure on the molar volumes of wüstite ( $\text{Fe}_{0.92}\text{O}$ ) and three spinel phases of  $\text{Fe}_2\text{SiO}_4$ ,  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$  and  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$  has been determined by means of the X-ray diffraction method at pressures up to 255 kb at room temperatures. The isothermal bulk moduli for these minerals have been evaluated at zero pressure from the volume data by a least-squares fit to the Birch equation. The value for wüstite thus determined is  $1.42 \pm 0.10$  Mb. The values for the spinel phases of olivines range between 1.96 and  $2.12 \pm 0.10$  Mb and are indistinguishable from each other. The mean volume thermal expansivity for the spinel phase of  $\text{Fe}_2\text{SiO}_4$  has been determined to be  $(23 \pm 1) \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  at a pressure of 1 bar and a temperature range of  $8^\circ\text{--}396^\circ\text{C}$  by means of the X-ray diffraction technique. On the basis of these data, the stability boundary for an assumed reaction,  $\text{Fe}_2\text{SiO}_4$  (spinel) =  $2 \text{ FeO(wüstite)} + \text{SiO}_2(\text{stishovite})$ , has been estimated to be  $P \text{ (kb)} = 227.5 - 0.022 T \text{ (}^\circ\text{C)}$ .

### INTRODUCTION

For depths between 350 and 700 km in the earth's mantle, the seismic wave velocities increase with depth at a far greater rate than expected from the simple compression of ferromagnesian silicate minerals commonly found in the earth's crust. This has been interpreted by Birch [1952] to be the result of phase transformations occurring in the rock forming minerals. More recently, Anderson [1967] has demonstrated that the observed stepwise increase in the seismic wave velocities in the C region (365–700 km) of the mantle can be accounted for by two sets of phase transformations, olivine-spinel and spinel-post spinel. In his study, some thermodynamic parameters, in particular the change in volume associated with the phase transformations, were estimated on the basis of data obtained at atmospheric pressure owing to a lack of volume data determined at high pressures. However, the thermodynamic stability relationships among the possible mantle minerals could be calculated with greater confidence if reliable volume data were available.

The purpose of this paper is to report measurements of the effect of pressure on the lattice

parameters, hence volumes, of the spinel phases of  $\text{Fe}_2\text{SiO}_4$ ,  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$  and  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$  and of wüstite at room temperature and measurements of the effect of temperature on the volume of the spinel phase of  $\text{Fe}_2\text{SiO}_4$  at 1 bar obtained by means of X-ray diffraction techniques. The results will be used to calculate the thermodynamic stability range for the spinel phase.

### SAMPLES

The samples of the spinel phases of  $(\text{Fe}, \text{Mg})_2\text{SiO}_4$  used for the present study are the quench products prepared at 60–70 kb and  $800\text{--}900^\circ\text{C}$ . The molar volumes of these samples have been determined to be  $42.03 \pm 0.02 \text{ cm}^3/\text{mole}$  for  $\text{Fe}_2\text{SiO}_4$ ,  $41.86 \pm 0.02 \text{ cm}^3/\text{mole}$  for  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$ , and  $41.57 \pm 0.03 \text{ cm}^3/\text{mole}$  for  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$  at 1 bar and  $25^\circ\text{C}$  by means of the Debye-Scherrer X-ray diffraction technique.

The wüstite sample was prepared by thermal decomposition of  $\text{Fe}_2\text{C}_2\text{O}_4$  under a controlled oxygen atmosphere at  $835^\circ\text{C}$ . The lattice parameter of the wüstite thus formed is 4.289 Å at room temperature and 1 bar pressure, and the molar volume is  $11.88 \pm 0.03 \text{ cm}^3/\text{mole}$ . Its chemical composition is estimated to be  $\text{Fe}_{0.92}\text{O}$  on the basis of the relationship given by Wells

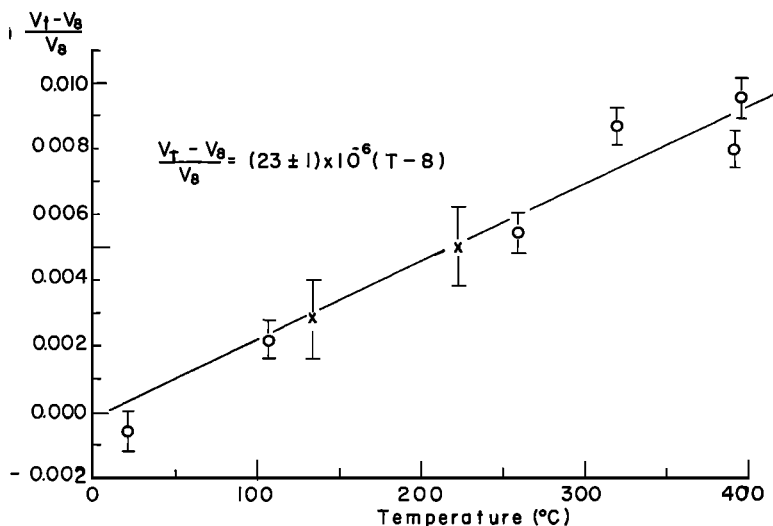


Fig. 1. The thermal expansion of the  $\text{Fe}_2\text{SiO}_4$  phase in a temperature range of 8° to 396° at 1 bar pressure. The circles indicate the measurements obtained from the (440) diffraction line; the crosses indicate values obtained from the (311) diffraction line. The mean volume thermal expansivity was calculated to be  $(23 \pm 1) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  by a least-squares fit to  $V_T = V_8[1 + \alpha(T - 8)]$ , where  $T$  is expressed in degrees Celsius.

[1950, p. 382]  $a$  (Å) =  $0.5826x + 3.7507$ , where  $a$  is the lattice parameter and  $x$  is the atomic ratio in the form of  $\text{Fe}_x\text{O}$ .

#### THERMAL EXPANSION

The thermal expansion of the spinel phase of the  $\text{Fe}_2\text{SiO}_4$  sample was determined in a temperature range of 8 to 396°C and at 1 bar pressure by means of an X-ray diffractometer (GE XRD-5) equipped with a heating stage similar to the design of *Skinner et al.* [1962]. The

TABLE 1. Mean Thermal Expansion Coefficients between 20 and 400°C for Various Spinel Group Minerals

Mineral Names	Chemical Composition	Mean Thermal Expansion Coefficient at 1 bar ( $10^{-6} \text{ }^\circ\text{C}^{-1}$ )
Cromite	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$	12.7*
Hercynite	$\text{FeO} \cdot \text{Al}_2\text{O}_3$	19.9*
Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	23.9*
Magnetite	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	35.5*
Spinel phase of Fayalite	$\text{Fe}_2\text{SiO}_4$	$23 \pm 1$ †

\* These values were calculated from the data listed in the *Handbook of Physical Constants*, [1966].

† Temperature range between 8° and 396°C.

angles for the (311) and (440) diffraction lines produced by  $\text{FeK}_{\alpha 1}$  radiation were measured to within 0.005°. The temperature was measured to  $\pm 1^\circ\text{C}$  with a chromel-alumel thermocouple. The hot junction was embedded in the sample holder to eliminate the effect of direct radiation from the heating elements. After 2 hours at 390°C, no evidence of decomposition or phase transformation was observed. The results of two sets of experiments are shown in Figure 1. The mean thermal expansivity,  $\Delta V/V_0 \cdot \Delta T$ , was determined to be  $(23 \pm 1) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . This value is compared with values for other spinel minerals in Table 1. The result of the present work appears to be consistent with the values reported for other types of spinel minerals.

#### EFFECT OF PRESSURE

The effect of pressure on the volumes of the spinel phases of  $(\text{Fe}, \text{Mg})_2\text{SiO}_4$  and wüstite was determined up to 255 kb at room temperature by means of the X-ray diffraction technique developed by *Bassett et al.* [1967]. A powdered specimen was compressed between diamond anvil faces with a diameter of approximately 0.3 mm and was exposed to a finely collimated X-ray beam (0.05 mm diameter) of molybdenum  $\text{K}_{\alpha 1}$  radiation monochromatized by a

curved quartz crystal. The X-ray beams diffracted by the sample were recorded on a cylindrical photographic film whose center coincides exactly with the sample. This diffraction apparatus has essentially the geometry of the Debye-Scherrer camera. Since the pressure gradient in the sample compressed between the diamond anvils is minimum in the central area of the sample, the X-ray beam was directed to the center of the anvil area to minimize the effect of the pressure gradient on the determination of the lattice parameters. The pressure to which the sample was subjected was determined by means of a NaCl internal pressure standard mixed intimately with the powdered specimen. Each photographic record consists of the diffraction lines of the sample and NaCl. The volume of the sample and the pressure was computed from the 'd' values by assuming that the sample was at the same pressure as the NaCl. The (311), (400), (333), (511) and (440) diffraction lines for the spinel phase, the (111), (200) and (220) diffraction lines for wüstite, and the (200) and (220) diffraction lines for NaCl were used for the computations. The lattice parameter values reported in this paper are accurate to  $\pm 0.1\%$ , and hence the volume values are accurate to  $\pm 0.3\%$ .

The pressure-volume relationship for NaCl was calculated from the Hildebrand and Mie-Grüneisen equations [Fumi and Tosi, 1962].

The pressure values calculated from these equations are sensitive to the value chosen for the isothermal bulk modulus at zero pressure  $K_0$ . Since the value of  $K_0$ ,  $237.5 \pm 1.5$  kb, obtained by Slagle and McKinstry [1967] and Haussuhl [1960] appears to be superior to the values adopted by Decker [1965, 1966] and by Perez-Albuerne and Drickamer [1965], their  $K_0$  value was adopted. The pressure-volume relationship is insensitive to the particular form of vibrational energy used, since the pressures calculated from the Hildebrand equation agree with those calculated from the Mie-Grüneisen equation to within  $\pm 1\%$  for pressures up to 300 kb. Since the Hildebrand equation is easier to compute, it was adopted for the conversion of NaCl volume to pressure. Table 2 compares the results of the present calculation with those of other workers and with the results of experimental studies of the compression of NaCl. It should be noted that the results of Decker's recalculation (personal communication, 1968) of the Mie-Grüneisen equation for NaCl using a  $K_0$  value of 237.0 kb (based on three recent determinations by Slagle and McKinstry [1967], by Chang [1965], and Drabble and Strathen [1967]) yields pressures within 1% of the present calculation. These results indicate that the effect of repulsion between second nearest neighbors (included in Decker's treatment) is small. The total uncertainty in the pressure values resulting from

TABLE 2. Pressure-Volume Relationships for the B1 Phase of NaCl

References	T, °C	V/V <sub>0</sub> , kb						Methods
		1.00	0.90	0.80	0.75	0.70	0.65	
Decker [1965, 1966]	25	0	31	87	132	190	273	Modified Mie-Grüneisen equation with $B_0 = 234.2$ kb
Decker (personal communication, 1968)	25	0	33	90	136	198	287	Same as above, but with $B_0 = 237.0$ kb
Anderson [1965]	25	0	32	100	160	250	400	Murnaghan trajectory with $B_0 = 234.2$ kb and $B'_0 = 5.35$ .
Perez-Albuerne and Drickamer [1965]	25	0	33	93	140	205	294	Hildebrand equation
Frütz et al. [1967]	25	0	...	...	137	200	...	Shock Hugoniot corrected for temperature
This work	25	0	33	92	138	202	290*	Hildebrand equation with $B_0 = 237.5$ kb and $B'_0 = 5.35$ .
Al'tshuler et al. [1960]	Hug.	0	32	94	145	210	325	Shock Hugoniot
Lombard [1961]	Hug.	0	32	94	145	210	325	Shock Hugoniot

\* The B1(sodium chloride structure)-B2(cesium chloride structure) phase transformation occurs at a pressure of 300 kb at 25°C [Bassett et al., 1968].

TABLE 3. Effect of Pressure on the Molar Volumes of Wüstite and the Spinel Phases of  $(\text{Fe, Mg})_2\text{SiO}_4$  at Room Temperature

Run	NaCl		P, kb	Wüstite ( $\text{Fe}_{0.92}\text{O}$ )		
	a, A	$V/V_0$		a, A	$V, \text{cm}^3/\text{mole}$	$V/V_0$
DS	5.640	1.000	0	4.289	11.88	1.000
5LD36	5.260	0.811	83	4.223	11.34	0.955
3LD107	5.053	0.719	174	4.159	10.83	0.912
3LD106	4.964	0.682	230	4.111	10.46	0.881
3LD97	4.937	0.671	249	4.100	10.37	0.873
1LD379	4.935	0.670	251	4.097	10.35	0.872
3LD93	4.928	0.667	256	4.092	10.31	0.868

Spinel ( $\text{Fe}_2\text{SiO}_4$ )						
DS	5.640	1.000	0	8.234	42.03	1.000
8UP6	5.640	1.000	0	8.231	41.99	0.999
3LD81	5.622	0.990	2	8.236	42.06	1.001
3LD80	5.295	0.828	72	8.160	40.91	0.973
8UP5	5.280	0.820	77	8.137	40.56	0.965
3LD82	5.086	0.733	156	8.057	39.37	0.937
3LD83	5.029	0.709	189	8.026	38.92	0.926
8UP21	5.023	0.706	192	8.025	38.91	0.926
8UP10	5.020	0.705	193	8.018	38.81	0.923
8UP8	4.982	0.689	217	7.997	38.50	0.916
8UP22	4.942	0.673	245	7.973	38.16	0.908
8UP23	4.929	0.668	255	7.974	38.17	0.908

Spinel ( $\text{Fe}_{1.8}\text{Mg}_{0.2}$ ) $\text{SiO}_4$						
DS	5.640	1.000	0	8.223	41.86	1.000
15UP8	5.166	0.768	119	8.079	39.70	0.948
7UP42	5.082	0.732	159	8.035	39.05	0.933
1LD380	5.072	0.727	162	8.026	38.92	0.930
7UP43	5.023	0.706	192	8.003	38.59	0.922
1LD381	5.012	0.702	198	7.983	38.30	0.915
16UP4	5.005	0.699	201	7.976	38.20	0.913

Spinel ( $\text{Fe}_{1.6}\text{Mg}_{0.4}$ ) $\text{SiO}_4$						
DS	5.640	1.000	0	8.204	41.57	1.000
5LD32	5.616	0.987	3	8.190	41.37	0.995
5LD33	5.296	0.828	72	8.120	40.31	0.970
3LD98	5.267	0.814	81	8.108	40.13	0.965
3LD90	5.052	0.719	175	8.012	38.73	0.932
3LD99	5.003	0.698	205	7.975	38.18	0.918
3LD92	4.991	0.693	211	7.981	38.27	0.921
3LD91	4.976	0.687	222	7.954	37.88	0.911

uncertainties in the individual parameters used in the Hildebrand equation is  $\pm 2\%$ . On the other hand, an uncertainty of  $\pm 0.3\%$  in volume measurements of NaCl would result in uncertainties of  $\pm 2$  kb at 100 kb and  $\pm 4$  kb at 300 kb in pressure determinations. Therefore, the pressure values reported in this paper have a precision of  $\pm 2\%$  at 100 kb and  $\pm 1\%$  at 300

kb but have an accuracy of  $\pm 3-4\%$  in a pressure range of 100 to 300 kb.

The experimental data for the effect of pressure on the molar volumes of the spinel phases of  $(\text{Fe, Mg})_2\text{SiO}_4$  and wüstite at room temperature are listed in Table 3, and are graphically shown in Figures 2 and 3. The present data for wüstite are in agreement within the experimental uncertainties with those obtained by *Clendenen and Drickamer* [1966], when their data are corrected to the pressure scale used in the present work.

The isothermal bulk modulus at zero pressure was determined by means of the least-squares fit of the experimental data to the Birch equation

$$P = \frac{2}{3}K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}] \cdot \{1 - \xi[(V_0/V)^{2/3} - 1]\}$$

where  $K_0$  is the isothermal bulk modulus evaluated at zero pressure,  $V_0$  and  $V$  are the volume at zero pressure and pressure  $P$ , respectively, and  $\xi$  is a dimensionless parameter. Since the present volume data are not precise enough to permit a satisfactory determination of the  $\xi$  parameter, it was assumed to be zero, and the bulk modulus values were calculated by means of the resulting one-parameter Birch equation.

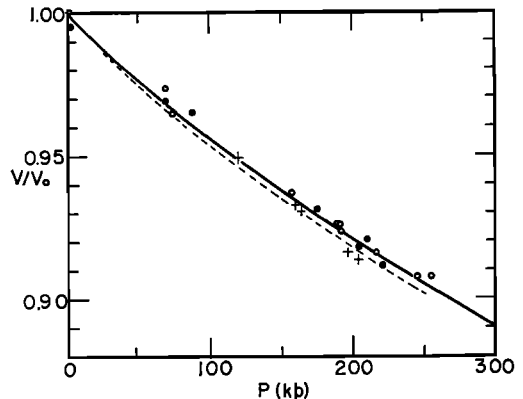


Fig. 2. Isothermal compression of the three spinel phases of  $(\text{Fe}\cdot\text{Mg})_2\text{SiO}_4$  at room temperature. The experimental data are indicated by open circles for  $\text{Fe}_2\text{SiO}_4$ , crosses for  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$ , and closed circles for  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$ . The solid curve is the least-squares fit of the data for  $\text{Fe}_2\text{SiO}_4$  and  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$  to the Birch equation ( $\xi = 0$ ) and corresponds to  $K_0 = 2.1$  Mb. The broken line indicates the least-squares fit of the data for  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$  to the same equation and corresponds to  $K_0 = 1.96$  Mb.

The results of the calculations are shown in Table 4. The bulk moduli for the three spinel phases are indistinguishable from each other and are about 2.1 Mb.

COMPARISON WITH THE SHOCK COMPRESSION DATA

The results of the present work on the Fe<sub>2</sub>SiO<sub>4</sub> spinel are plotted in Figure 4 along with the isothermal compression data of fayalite obtained by Adams [1931] and the shock Hugoniot data for the Rockport fayalite obtained by McQueen and Marsh [1966]. An extrapolation of the present data to higher pressures was made by means of the Birch equation. It is observed that the pressure-volume relationship for a spinel phase of Fe<sub>2</sub>SiO<sub>4</sub> is distinctly different from that obtained by the shock experiments at pressures higher than 580 kb. The observed discrepancy indicates that the material under the shock loading is not in the spinel phase but must be in a denser phase or an assemblage of denser phases than the spinel. In an attempt to explain the shock data, it was assumed that fayalite was decomposed to a mineral assemblage of stoichiometric wüstite (FeO) and stishovite (SiO<sub>2</sub>). The pressure-volume relationship for this assemblage at 25°C was assumed to be the algebraic sum of the volumes of the respective phases. For this purpose, the equa-

TABLE 4. Values of the Isothermal Bulk Modulus (in Megabars) at Room Temperature Determined by a Least-Square Fit of the Experimental Data to the Birch Equation with  $\xi = 0$

Wüstite	Spinel Phase of (Fe, Mg) <sub>2</sub> SiO <sub>4</sub>			
	Fe <sub>0.921</sub> O	Fe <sub>2</sub> SiO <sub>4</sub>	Fe <sub>1.8Mg<sub>0.2</sub></sub> SiO <sub>4</sub>	Fe <sub>1.8Mg<sub>0.2</sub></sub> SiO <sub>4</sub>
1.42 ± 0.10	2.12 ± 0.10	1.96 ± 0.10	2.08 ± 0.10	

tions of state for wüstite previously presented and for stishovite determined by McQueen et al. [1963] were used. As shown in Figure 4, the 25°C isotherm for this mineral assemblage coincides closely with the shock compression data. This result suggests that the spinel was either decomposed to this mineral assemblage under the shock condition or transformed to another high pressure polymorph for which the pressure-volume relationship is similar to the relationship for the mineral assemblage.

THERMODYNAMIC CONSIDERATIONS

Since the effect of pressure on the molar volumes of the polymorphs of Fe<sub>2</sub>SiO<sub>4</sub> and its component oxides is now known at room temperature, the thermodynamic relationships among those phases can be calculated with the equation

$$\Delta F_T^P - \Delta F_T^0 = \int_0^P V_T dP$$

where  $\Delta F_T^P$  and  $\Delta F_T^0$  are the Gibbs free energies at temperature  $T$  and at pressures  $P$  and zero, respectively, and  $V_T$  is the volume of the given phase at temperature  $T$ . The standard Gibbs free energy of formation for the spinel phase of Fe<sub>2</sub>SiO<sub>4</sub> can be then expressed by

$$\Delta F_{298}^0(\text{spinel}) = \Delta F_{298}^0(\text{olivine}) - \int_0^{P^*} [V(\text{spinel}) - V(\text{olivine})] dP$$

where the parentheses after  $\Delta F$  and  $V$  indicate the phases, and  $P^*$  is the equilibrium pressure for the phase transformation at 298°K.

The value for the standard Gibbs free energy of formation of fayalite has been determined by King [1952] to be  $-7.28 \pm 0.5$  kcal for the following reaction:

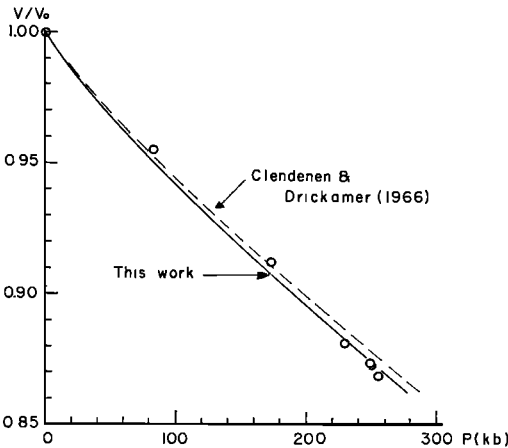
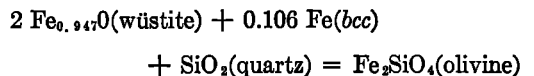


Fig. 3. The isothermal compression of wüstite (Fe<sub>0.921</sub>O) at room temperature. The least-squares fit of the present data to the Birch equation ( $\xi = 0$ ) is indicated by the solid curve, and the fit of the data obtained by Clendenen and Drickamer [1966] is indicated by the broken curve.

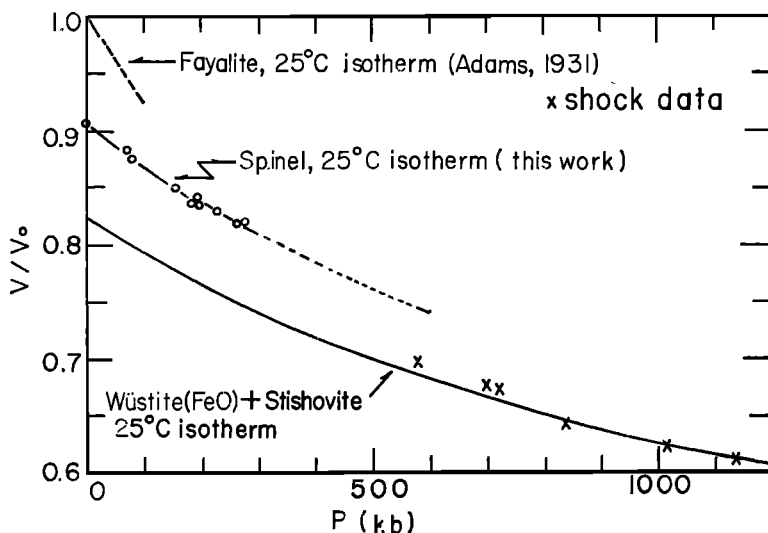


Fig. 4. Summary of the compression data for the various phases of  $\text{Fe}_2\text{SiO}_4$ . The circles indicate the results of this work, and the crosses indicate the results of shock compression for fayalite (Rockport, Massachusetts) obtained by *McQueen and Marsh* [1966]. The discrepancy between the spinel data and the shock data indicates that fayalite is not in the spinel phase under shock loading. The solid curve through the shock compression data represents an algebraic sum of the volumes of wüstite and stishovite. Close agreement between the volume of this assemblage and the shock data suggests that the spinel phase may decompose to this assemblage at high pressures.

The thermodynamic stability boundary between fayalite and the spinel phase has been determined by *Akimoto and Komada* [1967] in a pressure-temperature range of 40–70 kb and 700–1500°C. Their pressure apparatus was calibrated with reference to three phase transformations, Bi I–II (25.4 kb), Tl II–III (36.7 kb), and Ba I–II (59 kb), reported by *Kennedy and LaMori* [1962]. More recently, *Haygarth et al.* [1967] have redetermined the transformation pressure for Ba I–II by means of a single stage piston-cylinder apparatus and reported a value of  $55.0 \pm 0.5$  kb at 22°C. On the other hand, *Jeffery et al.* [1966], by using X-ray diffraction employing a tetrahedral press, determined the same phase transformation in barium and reported a value of  $53.3 \pm 1.2$  kb at room temperature on the basis of the NaCl pressure scale proposed by *Decker* [1965, 1966]. However, this discrepancy can be eliminated if the pressure-volume relationship for NaCl reported in the present work is used instead of Decker's to calculate the pressure from the data of *Jeffery et al.*, [1966]. When this correction is made, a value of  $55.2 \pm 1.2$  kb for the barium transformation is obtained. The value is now in ex-

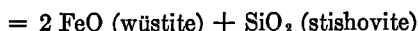
cellent agreement with the result of *Haygarth et al.* [1967]. Accordingly, the data of *Akimoto and Komada* [1967] for the fayalite-spinel transformation were revised on the basis of the pressure value for the Ba I–II transformation obtained by *Haygarth et al.* and are expressed by the equation

$$P \text{ (kb)} = 25.5 + 0.026T \text{ (}^\circ\text{C)}$$

This revised equation is internally consistent with the pressure scale used in the present work and yields a value of 26 kb for the olivine-spinel transformation at 25°C. Thus, the difference in the standard free energies of the spinel and olivine phases can be calculated from the equation above to be  $2.6 \pm 0.3$  kcal. The uncertainty is estimated on the basis of a  $\pm 3$ -kb uncertainty in the phase boundary linearly extrapolated down to 25°C.

The shock compression data shown in Figure 4 indicate that at high pressures  $\text{Fe}_2\text{SiO}_4$  spinel transforms to either a single high pressure phase or an assembly of phases. If the spinel phase is assumed to undergo the following chemical reaction

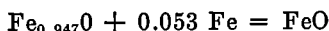
Fe<sub>2</sub>SiO<sub>4</sub> (spinel)



the pressure at which the free energy difference between the two sides becomes zero can be calculated to be 227 kb at 25°C on the basis of the thermodynamic data listed in Table 5. The thermodynamic data for stoichiometric wüstite (FeO) were estimated on the basis of the experimental results obtained by *Katsura et al.* [1967] that stoichiometric wüstite is more stable than the iron deficient wüstite under high pressures above 36 kb at 770°C. Assuming that the equilibrium boundary at 25°C is at 10 ± 10 kb, the difference in Gibbs free energy and in entropy for the following reaction has been calculated to be

$$\Delta F_{298}^{\circ} = 0.06 \pm 0.06 \text{ kcal}$$

$$\Delta S_{298}^{\circ} = -0.08 \pm 0.08 \text{ cal/deg}$$



$$\Delta V_{298} = -0.25 \text{ cm}^3$$

The effect of temperature on the equilibrium pressure for the decomposition of the spinel phase to component oxides can be calculated by the Clapeyron equation,  $dP/dT = \Delta S/\Delta V$ , in which  $\Delta S$  and  $\Delta V$  are respectively the entropy and volume change for the reaction at an equilibrium pressure-temperature condition. At room temperature, the volume change for the reaction can be evaluated to be -3.20 cm<sup>3</sup> at 227 kb on the basis of the data shown in Figure 4.

For the calculation of the entropy change for the reaction at room temperature, the effect of pressure on the entropies of each phase must be taken into account. This can be estimated through the equation

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$$

Integration of this equation at a constant temperature yields

$$\int_{S_0}^{S_P} dS = - \int_0^P (\partial V/\partial T)_P dP$$

and

$$\alpha = (1/V)(\partial V/\partial T)_P$$

where  $\alpha$  is the volume thermal expansivity and  $S_P$  is the entropy at pressure  $P$ . On the other

hand,  $\alpha$  may be related to other thermodynamic parameters  $\alpha = \gamma Cv/VK$ , where  $\gamma$  is the Grüneisen parameter,  $Cv$  is the heat capacity at constant volume, and  $K$  is the isothermal bulk modulus. A combination of these three equations yields

$$\int_{S_0}^{S_P} dS = - \int_0^P (\gamma Cv/K) dP$$

In this equation, the Grüneisen parameter is assumed to be a function of volume alone. Thus, both  $\gamma$  and  $K$  can be expressed as a function of pressure through the equation of state. Furthermore, if the Fe<sub>2</sub>SiO<sub>4</sub> spinel phase is assumed to be a Debye solid,  $Cv$  can be related to entropy  $S$  through the Debye function (eg., see *Mao* [1967]). Therefore, the right-hand side of the above equation can be expressed as a function of  $S$  and  $P$ , and the value of  $S_P$  can be calculated from a numerical integration of the equation. However, since the volume dependence on  $\gamma$  is not well known, two types of functions  $\gamma/V^{1/3} = \text{constant}$  and  $\gamma/V = \text{constant}$  were assumed in performing the calculations. The results of the calculations are summarized in Table 6. It is seen that the entropy change for the reaction is insensitive to the assumptions made for  $Cv$  and  $\gamma$  and that the pressure correction amounts to about 25% of the entropy change at zero pressure. The univariant stability

TABLE 5. Thermodynamic Data used for the Calculation of the Stability Boundary for Fe<sub>2</sub>SiO<sub>4</sub>(spinel) = FeO (wüstite) + SiO<sub>2</sub>(stishovite)

	$\Delta F_{298}^{\circ}$ , kcal/mole	$V_0$ , cm <sup>3</sup> /mole	$K_0$ , Mb	$S_{298}^{\circ}$ , cal/ mole·deg
Fayalite,*				
Fe <sub>2</sub> SiO <sub>4</sub>	-7.28	46.39	1.10	34.70
Spinel, Fe <sub>2</sub> SiO <sub>4</sub>	-4.7 ± 0.3	42.03	2 12 ± 0.10	32 4 ± 0.4
Stishovite, SiO <sub>2</sub>	12.7 ± 0.3 †	14.02*	4.28 †	6.64 †
Wüstite, FeO	0.06 ± 0.06	12.17 ‡	1.42 ± 0.10	14 0 ± 0.08

The values of  $\Delta F_{298}^{\circ}$  are expressed in reference to wüstite (Fe<sub>0.947</sub>O), iron (bcc) and quartz (SiO<sub>2</sub>). The bulk modulus for stoichiometric wüstite is assumed to be same as that for wüstite (Fe<sub>0.947</sub>O).

\* *Clark* [1966].

† *Holm, et al.* [1967].

‡ Calculated from the data presented in *McQueen et al.* [1963].

§ *Katsura et al.* [1967].

TABLE 6. Entropy Change for the Reaction,  $\text{Fe}_2\text{SiO}_4(\text{spinel}) = 2\text{FeO}(\text{wüstite}) + \text{SiO}_2(\text{stishovite})$ , at 227 kb and 25°C

		$\gamma \propto V^{\frac{1}{3}}$ $Cv = D(S)$	$\gamma \propto V$ $Cv = D(S)$	$\gamma \propto V^{\frac{1}{3}}$ $Cv = \text{const.}$	$S^p = S^o$
$\int_{p=0}^{227} dS$ , cal/mole·deg	Spinel, $\text{Fe}_2\text{SiO}_4$	-3.61	-3.51	-3.64	...
	Stishovite, $\text{SiO}_2$	-0.47	-0.46	-0.48	...
	Wüstite, FeO	-1.85	-1.81	-1.89	...
$\Delta S$ , cal/deg		1.68	1.67	1.62	2.24
$(dP/dT) = \Delta S/\Delta V$ , kb/°C		0.022	0.022	0.021	0.029

The effect of pressure on entropies of each phase was calculated under the different assumptions made for  $Cv$  and  $\gamma$ .  $Cv = D(S)$  indicates that  $Cv$  is related to entropy  $S$  through the Debye function. Because of the lack of experimental data, it was assumed that the thermal expansivity and isothermal bulk modulus for stoichiometric FeO are equal to the respective values for  $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.924}\text{O}$ . A value of  $-3.2 \text{ cm}^3$  at 227 kb was used for the  $\Delta V$  value for the reaction.

boundary thus calculated for the decomposition of the  $\text{Fe}_2\text{SiO}_4$  spinel phase to wüstite and stishovite is

$$P \text{ (kb)} = 227.5 - 0.022T \text{ (}^\circ\text{C)}$$

If the slope of the univariant boundary is assumed to be independent of temperature and pressure, the  $\text{Fe}_2\text{SiO}_4$  spinel phase should decompose to its respective oxides at a depth of about 455 km in the earth where the temperature is assumed to be 1800°C.

#### SUMMARY AND CONCLUSIONS

Effect of pressure on the molar volume of wüstite ( $\text{Fe}_{0.924}\text{O}$ ) and the spinel phases of  $\text{Fe}_2\text{SiO}_4$ ,  $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{SiO}_4$  and  $\text{Fe}_{1.6}\text{Mg}_{0.4}\text{SiO}_4$  has been measured by the X-ray diffraction method at pressures up to 255 kb at room temperature. The isothermal bulk moduli at zero pressure were evaluated by the least-squares fit of the volume data to the Birch equation. The values thus determined are  $1.42 \pm 0.10 \text{ Mb}$  for wüstite, and  $2.1 \pm 0.1 \text{ Mb}$  for the three spinel phases.

The mean volume thermal expansivity for the  $\text{Fe}_2\text{SiO}_4$  spinel phase has been determined by the X-ray diffraction technique to be  $(23 \pm 1) \times 10^{-8} \text{ }^\circ\text{C}^{-1}$  between 8 and 396°C at 1 bar pressure.

The univariant stability boundary for the reaction  $\text{Fe}_2\text{SiO}_4(\text{spinel}) = 2\text{FeO}(\text{wüstite}) + \text{SiO}_2(\text{stishovite})$  has been calculated to be  $P \text{ (kb)} = 227.5 - 0.022T \text{ (}^\circ\text{C)}$  on the basis of the room temperature data. If this boundary can be extrapolated linearly to high temperatures, the  $\text{Fe}_2\text{SiO}_4$  spinel phase should decompose to

its respective oxides at a depth of about 455 km in the earth where the temperature is assumed to be 1800°C.

*Acknowledgments.* We are grateful to P. Stook and Jeng-Yih Guu for their technical assistance and to Daniel L. Decker of Brigham Young University for providing the results of his recalculations for the equation of state of NaCl.

This research was financially supported by grant GP-5304 from the National Science Foundation.

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(Received July 17, 1968;  
revised September 19, 1968.)