In Situ Observation of the Olivine-Spinel Phase Transformation in Fe_2SiO_4 Using Synchrotron Radiation

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Detailed in situ observations of the olivine-spinel phase transformation in Fe_2SiO_4 were performed using a cubic anvil type of high-pressure and high-temperature X ray diffraction apparatus combined with synchrotron radiation. An accurate equilibrium phase boundary, density increase at the transition, and thermal expansion of spinel phase were determined as follows: Transition pressure P (GPa) = 2.75 $+ 2.5 \times 10^{-3} \ T$ (°C); $\Delta\rho$ at 5.3 GPa and 1000°C = 9.5%; mean volume expansion between 25°C and 1000°C at 5.3 GPa = $2.0 \times 10^{-5} \ K^{-1}$. Comparisons of the observed and calculated equilibrium phase boundaries indicate that when the effect of cation disorder is taken into account, the observed phase boundary becomes consistent with thermochemical data. The thermal expansion of the spinel phase observed in its stable field differs significantly from that observed at atmospheric pressure. Nonuniform formation of the diffraction peaks of the spinel phase was not observed in the present study, which indicates that the mechanism of the olivine-spinel transition may depend on the stress state of the specimen.

INTRODUCTION

The olivine(α)-spinel(γ) transformation in (Mg, Fe)$_2$SiO$_4$ is regarded as playing an important role in the formation of seismic discontinuities and in the behavior of subducting slabs in the earth's mantle. Therefore its various parameters such as transformation pressure, kinetics, and density increase associated with the transformation are important factors in modeling the structure of the upper mantle.

Numerous studies on Fe_2SiO_4 have been performed to clarify the nature of the olivine-spinel transformation using either quench technique [Akimoto et al., 1965, 1967] or in situ X ray observations [Inoue, 1975; Sung and Burns, 1976; Furnish and Bassett, 1983]. Many problems, such as the determination of precise equilibrium phase boundary and equations of state of the high-pressure phase, are, however, still left unsolved. In situ X ray observation provides us much more information than do quench experiments on the behavior of minerals under pressure. Limited intensity and large divergence of conventional X ray sources, however, make it difficult to get detailed information because these result in long exposure times, low resolution, and low signal to noise ratio of the X ray measurement. The use of synchrotron radiation has relieved these difficulties dramatically [Yagi et al., 1985, 1987].

The purpose of the present study is to make detailed in situ

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X ray observations of the olivine-spinel phase transition in Fe_2SiO_4 using a cubic anvil type of high-pressure and high-temperature apparatus combined with synchrotron radiation. The equilibrium phase boundary, density increase at the transition, thermal expansion under high pressure, and some information on the kinetics of the transition were obtained from the analysis of the present experimental data.

EXPERIMENTAL DATA

Experiments were performed using "MAX-80," a multianvil type of high-pressure and high-temperature X ray diffraction apparatus combined with the "Photon Factory," a synchrotron radiation source at the National Institute for High Energy Physics (KEK) in Tsukuba. MAX-80 consists of a cubic anvil type of high-pressure vessel, a 500-ton hydraulic press, and an energy dispersive type X ray diffraction system. Details of the apparatus are described elsewhere [Shimomura et al., 1984, 1985].

A sample assembly used for the present experiment is described in Figure 1. The powdered specimen was inserted in a sample chamber made of boron nitride and was placed in the lower half of a graphite furnace. The pressure marker was a mixture of sodium chloride, gold, and boron nitride and was placed in the upper half of the furnace. A boron nitride powder was mixed to prevent the grain growth of crystals. The furnace was then embedded in a pressure transmitting medium made of a mixture of amorphous boron and epoxy resin. The temperature was measured with a Pt/Pt-Rh13% thermocouple which was placed at the center of the furnace.

The incident X ray beam was 0.3 mm in height and approximately 0.5 mm in width, which was determined by the clearance between anvils. The position of the incident beam was monitored by observing the shadow profile of the direct beam and was adjusted close to the hot junction of the thermocouple so that the error in temperature measurement was minimized. In the present experiments the Photon Factory was usually operated at 2.5 GeV with a beam current from 150 to 70 mA. A typical exposure time for quantitative measurement was 200 or 300 s. A much shorter time was sufficient to check the initiation of the transition.
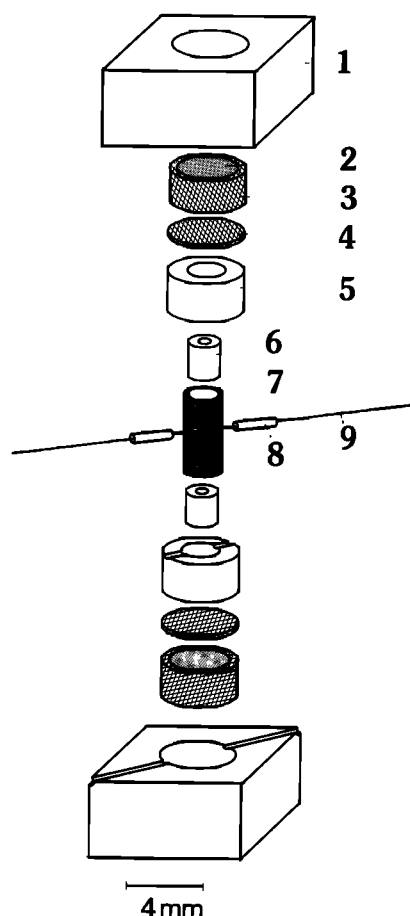
Fig. 1. Sample assembly for high-pressure and high-temperature in situ X ray observation. (1) Boron + epoxy resin pressure transmitting medium, (2) pyrophyllite end plug, (3) gold current ring, (4) molybdenum disk, (5) boron + epoxy resin sleeve, (6) boron nitride sample chamber, (7) graphite furnace, (8) ceramic insulation tube, and (9) Pt/Rh thermocouple.

The fayalite specimen was from the same batch of specimens used in the previous studies [*Yagi et al.*, 1974, 1975]. It was prepared from a mixture of hematite and silica heated at 1150°C in a CO_2-H_2 mixed gas. The powdered specimen thus prepared was finely ground and placed directly in a sample chamber made of boron nitride. In some runs, sodium chloride or boron nitride was mixed with the specimen to reduce stress concentrations and grain growth of the specimen.

Both isothermal and constant ram load paths were used in the present study. In isothermal experiments the specimen was heated to 800°C or 1000°C in the olivine stability field, and then pressure was increased while the temperature was kept constant. In constant ram load experiments the specimen was compressed to the spinel stability field at room temperature, and then temperature was increased while the ram load was kept constant. As will be discussed later, the onset of the transition was quite different between these two types of experiments.

Even when in situ observation is employed, the apparent phase boundary may be affected by the kinetics of the transition. Because of the limited experimental time, we may observe the phase which is not in equilibrium with the given PT condition. In order to overcome this difficulty, an equilibrium phase boundary was determined by comparing the relative stability of olivine and spinel at various PT conditions. At first, olivine starting material was partly transformed into spinel at 500°C or 600°C at about 5 GPa. This mixed phase was then kept at the desired PT condition for a certain period of time, and X ray measurements were made repeatedly to observe the change of two phases with time. An example of
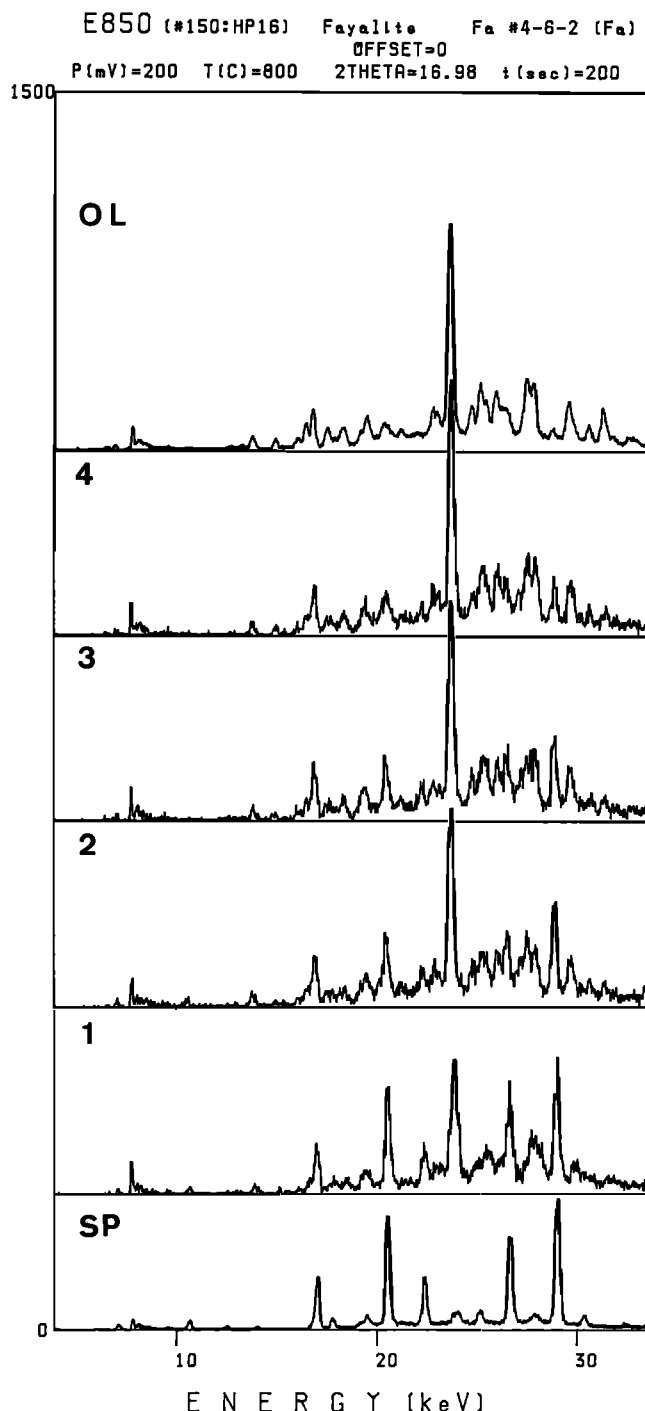

Fig. 2. Examples of X ray diffraction profiles. OL and SP are the diffraction patterns from single-phase olivine and spinel, respectively. Four spectra in between show a transition sequence from an olivine/spinel mixture into a single phase of olivine (from 1 to 4) which was observed at 5.1 GPa and 800°C. Exposure time for each diffraction was 200 s.

these observations is shown in Figure 2, in which a reverse reaction from olivine into spinel was clearly observed. The stability field of each phase was determined only when the relative change of the two phases was observed. The lattice parameter of the NaCl pressure standard was measured several times while the specimen was kept at the PT condition, and the pressure was calculated using Decker's equation of state for sodium chloride [Decker, 1971]. Two or three diffraction lines of NaCl, (200), (220), and (222), were used to calculate the lattice parameter. At room temperature and high pressure a systematic discrepancy was observed among lattice parameters calculated from different diffraction lines because of the nonhydrostatic stress in the specimen. Above 500°C, however, these discrepancies disappeared because sodium chloride became soft enough to give a quasi-hydrostatic environment.

Unit cell volumes of olivine and spinel phases of Fe_2SiO_4 were also measured. For the olivine phase, five to 11 lines (130), (022), (112), (210), (211), (132), (222), (240), (241), (004), and (062), were used for the calculation, and accuracy was about 0.5% because some of these lines were unresolved overlapping lines. The unit cell volume of the spinel phase was calculated from four or five lines, (311), (400), (331), (333), and (440), and was accurate to ±0.1%.

RESULTS AND DISCUSSION

Equilibrium Phase Boundary

Pressure and temperature data used to determine the phase boundary are summarized in Figure 3 and Table 1. Although X ray observations were made up to 1500°C, reduction of ferrous iron occurred at high temperature and reliable data were obtained only up to 1200°C. When a straight line is assumed for the equilibrium phase boundary between 800°C and 1200°C, it can be expressed by

$$P(\text{GPa}) = 2.75 + 2.5 \times 10^{-3} \, T(°C) \qquad (1)$$

Pressure values calculated from the present X ray measurements are accurate to ±0.04 GPa (Table 1). Uncertainty in the temperature measurement also affects the pressure value. Fortunately, however, $(dP/dT)_v$ of the sodium chloride pressure marker is 2.9×10^{-3} (GPa/deg) in this PT range and is close to the slope of the phase boundary determined in the present study (2.5×10^{-3} GPa/deg). Therefore even when the error in temperature measurement was as much as 50°C, which is an extreme case, the transition pressure is affected only by 0.02 GPa. Taking into account all these factors, the uncertainty of the transition pressure determined by the present study is estimated to be less than ±0.1 GPa, and equation (1) can be used as a reliable pressure calibration point between 800°C and 1200°C.

Comparisons of the present results with previous work are also made in Figure 3. It is clear that slopes of the boundary are similar to each other. The transition pressure is, however, about 0.7 GPa lower than that determined by Inoue [1975]. He used a cubic anvil type of high-pressure and high-temperature in situ X ray apparatus, similar to the present system. However, he determined the boundary mainly from the initiation pressure of the olivine-spinel transition in an isothermal compression. As will be discussed later, when a specimen is compressed isothermally, excess pressure is re-
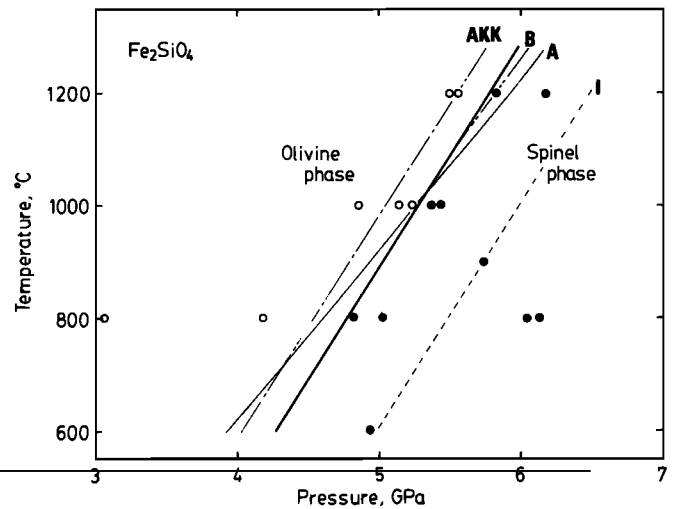

Fig. 3. Phase diagram of Fe_2SiO_4 and equilibrium phase boundary between olivine and spinel determined by the present study (thick solid line). Solid and open circles represent the PT conditions where the growth of spinel and olivine were observed, respectively. Thin lines are the phase boundaries reported by previous investigators: AKK, Akimoto et al. [1967] and I, Inoue [1975]; and A, calculated using thermochemical data without cation disorder, and B, calculated using thermochemical data including the effect of cation disorder.

quired to initiate the transition. Therefore it is reasonable that his boundary is higher than that obtained from the present experiment. This fact tells us that even when in situ observation is used, great care should be paid to the kinetics of the transition in order to obtain a reliable equilibrium phase boundary. In quench experiments [Akimoto et al., 1976], the temperature was raised after the specimen was compressed to a desired pressure. In this case the specimen transforms easily into its equilibrium phase. The small discrepancy between the quench experiment and the present result may be caused by the change of pressure in the sample chamber during heating. Since this effect is affected by many factors, such as the properties of the material used as a pressure transmitting medium, size of the furnace, pressure and temperature conditions, and so on, it is difficult to estimate the amount of this effect without using an internal pressure marker.

TABLE 1. PT Conditions of the Observations Near the Phase Boundary

Run	Temperature, °C	V/V_0 of NaCl	P, GPa
	$\alpha \rightarrow \gamma$ Transition		
4–12	800	0.9115(6)	5.02(2)
5–3	800	0.9164(13)	4.82(5)
16–4	800	0.9127(15)	4.97(6)
4–14	1000	0.9157(13)	5.44(5)
16–8	1000	0.9173(29)	5.37(11)
4–18	1200	0.9119(11)	6.18(4)
16–11	1200	0.9209(10)	5.82(4)
	$\gamma \rightarrow \alpha$ Transition		
4–10	800	0.9336(4)	4.18(1)
4–13	1000	0.9219(8)	5.18(3)
16–7	1000	0.9235(8)	5.14(3)
4–15	1200	0.9281(8)	5.56(3)
16–9	1200	0.9298(17)	5.50(6)

Read 0.9115(6) as 0.9115 ± 0.0006.

Comparison With Thermodynamic Calculations

The equilibrium phase boundary determined by the present study is also compared with the boundary calculated from thermodynamic data. The boundary calculation is made by the same method as used by *Akaogi et al.* [1984], using an enthalpy for the olivine-spinel transition of Fe_2SiO_4 of 2.9 ± 0.9 kJ/mol at 713°C [*Navrotsky et al.*, 1979], together with the equilibrium transition pressure of 5.25 GPa at 1000°C determined in this study. The effect of compression and thermal expansion on the molar volumes is corrected using the bulk moduli of the olivine and spinel phase by *Sumino* [1979] and *Sato* [1977], respectively, and thermal expansivity data at 5.3 GPa which are summarized in Table 3. The effect of temperature on the enthalpy and entropy of transition is also corrected using the heat capacity data of *Watanabe* [1982]. The entropy of transition obtained at 1000°C is -16.1 ± 0.7 J/mol K, and the calculated boundary is shown in Figure 3 (curve A). The boundary has a slight curvature in the temperature range of interest. The slope at 1000°C is $(3.2 \pm 0.2) \times 10^{-3}$ GPa/deg, which is larger than that of equation (1). However, the effect of cation disorder in spinel on the olivine-spinel transition boundary should also be taken into account for a more accurate calculation [*Navrotsky*, 1977]. The phase boundary calculation including this effect is made on the basis of the method of *Navrotsky* [1977]. The Fe-Si interchange enthalpy between tetrahedral and octahedral sites in the spinel structure is estimated from the Fe-Si disorder in Fe_2SiO_4 spinel observed by *Yagi et al.* [1974] and is used in the calculation. The boundary calculated including the disorder (curve B in Figure 3) shows a significant decrease of transition pressures at temperatures above about 1000°C compared with the boundary without the disorder (curve A). The average gradient of the boundary B at 1000°–1400°C is very close to that observed by the present study. From the above discussion, it could be concluded that the equilibrium boundary by equation (1) is consistent with the measured thermochemical data for the olivine-spinel transition in Fe_2SiO_4.

Density Increase Associated With the Transition

Unit cell volumes of α- and γ-Fe_2SiO_4 were measured at various PT conditions and are summarized in Table 2. From these results it is possible to compare the density increase associated with the transition at various conditions (Figure 4). At ambient condition, $(\rho_{SP} - \rho_{OL})/\rho_{OL}$ is calculated to be 10.4%. Using isothermal compression data of olivine and spinel at room temperature [*Yagi et al.*, 1977; *Sato*, 1977], this value decrease to 8.7% at 5.3 GPa and 25°C. The observed density increase during the transition at 5.3 GPa and 1000°C is calculated to be 9.5%. These figures together with other parameters associated with the transition are very important in discussions of olivine-spinel transitions and are summarized in Table 3.

Kinetics of the Transition

Initiation of the transition from the single phase of olivine was quite different, depending on the PT path of the experiment. When the specimen was compressed isothermally at 800°C or at 1000°C, the transition did not occur until the pressure exceeded more than 20% of the equilibrium transition pressure. On the other hand, the transition started much closer to the phase boundary when the specimen was com-

TABLE 2. Unit Cell Volumes of α- and γ-Fe_2SiO_4 at Elevated Pressures and Temperatures

Run	Temperature, °C	V/V_0 of NaCl	P, GPa	V, Å³
		α-Fe_2SiO_4		
3–5	1000	⋯	3.9*	307.2(10)
3–6	1000	0.9351(3)	4.72(1)	305.4(13)
3–7	1000	0.8985(9)	6.15(4)	302.0(16)
		γ-Fe_2SiO_4		
4–3	500	0.8848(2)	5.29(1)	548.7(6)
15–7	600	0.9142(4)	4.32(2)	552.4(3)
4–8	800	0.8858(3)	6.13(2)	550.4(15)
4–12	800	0.9115(6)	5.02(2)	552.6(7)
15–5	800	0.8862(25)	6.11(12)	551.0(4)
15–6	800	0.8826(9)	6.28(4)	549.3(5)
15–12	900	0.9053(25)	5.56(10)	551.3(17)
16–5	900	⋯	4.9*	555.6(6)
4–13	1000	0.9219(3)	5.18(3)	555.4(5)
4–13	1000	0.9219(3)	5.18(3)	555.7(4)
14–14	1000	0.9157(13)	5.44(5)	553.6(2)
16–8	1000	0.9173(29)	5.37(11)	556.1(3)
16–11	1200	0.9209(10)	5.82(4)	556.0(5)

Read 0.9351(3) as 0.9351 $\pm$ 0.0003.
*Estimated from the applied load.

pressed to the spinel field at room temperature and then subjected to increasing temperature. In this case the transition rate was also very fast even when the temperature was as low as 500°C. In this case, a delay of the transition was observed when soft materials such as boron nitride were mixed with the specimen.

Similar phenomena have been observed for the coesite-stishovite transition in SiO_2 [*Yagi and Akimoto*, 1976]. When fine-grained silica powder was compressed at room temperature and then heated, it transformed easily into stishovite via coesite, while much higher pressure and longer time was re-
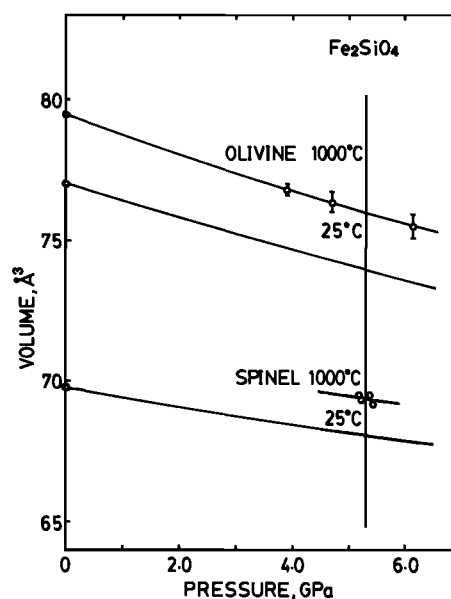

Fig. 4. Comparisons of isothermal compression curves of α- and γ-Fe_2SiO_4 at 25°C and at 1000°C. Vertical axis is the volume per molecule, and vertical line at 5.3 GPa indicates the transition pressure at 1000°C. Room temperature data for olivine and spinel are from *Yagi et al.* [1975] and from *Sato* [1977], respectively.

TABLE 3. Properties of α- and γ-Fe$_2$SiO$_4$

Transition Pressure	Value
P, GPa	$2.75 + 2.5 \times 10^{-3}T(°C)$

Density Increase Associated With Transition

PT Condition	ρ_{OL}, g/cm^3	ρ_{SP}, g/cm^3	$\Delta\rho$, %
0.1 MPa, 25°C	4.398†	4.851‡	10.3
5.3 GPa, 25°C	4.579†	4.971§	8.6
5.3 GPa, 1000°C	4.454	4.877	9.5

Thermal Expansion α at 0.1 MPa and at 5.3 GPa*

Phase	0.1 MPa	5.3 GPa
Olivine	3.3×10^{-5} (K^{-1})¶	2.9×10^{-5} (K^{-1})
Spinel	2.3×10^{-5} (K^{-1})‖	2.0×10^{-5} (K^{-1})

*Mean volume expansion is between 25 °C and 1000°C.
†Yagi et al. [1975].
‡Yagi et al. [1974].
§Sato [1977].
¶Suzuki et al. [1981].
‖Mao et al. [1969].

quired to form stishovite in isothermal compression at 1000°C. These results suggest that the kinetics of the transition is controlled not only by pressure and temperature but also by many other factors such as the stress state and grain size of the specimen. Unfortunately, it is impossible to control most of these factors in the present laboratory experiments. Although many studies have been made on the kinetics of the olivine-spinel transition in Fe$_2$SiO$_4$, so far only two parameters, pressure and temperature, have been used for the analysis. It is clear from the present result that in order to analyze the kinetics of the transition properly, many other factors are required. At this moment, it is dangerous to deduce definite conclusions from such laboratory experiments.

Mechanism of the Transition

Furnish and Bassett [1983] reported nonuniform formation of the diffraction peaks of the spinel phase. They observed the transition in Fe$_2$SiO$_4$ at 520°C while pressure was increased from 2 or 3 GPa to 7 GPa using a diamond anvil cell. On the basis of this observation they suggested a martensitic type mechanism for the olivine-spinel transition. Lauterjung and Will [1986] studied kinetics of the olivine-spinel transformation in the Mg$_2$GeO$_4$ using a belt-type apparatus combined with synchrotron radiation. They also reported that at the beginning of the transition only diffraction peaks from a spinel-type oxygen array were observed.

In the present experiment, no such behavior was observed. X ray observations were made repeatedly every 200 s, and even at the beginning of the transition, intensity ratios of the diffraction peaks of the spinel phase were unchanged. It is also clear from Figure 2 that when the spinel transforms into olivine, all the diffraction peaks of the spinel phase disappear in the same manner.

Many different ideas has been so far presented on the nature of the mechanism of olivine-spinel transition. Some of the experimental results indicated martensitic type of mecha-

nism, while others indicated diffusion type of mechanism. It is suggested that the type of mechanism is not unique, but it may vary with experimental conditions [Green, 1984]. In the present experiment the specimen was compressed isotropically by six anvils, and the deviatoric stress in the specimen is expected to be much less than the experiment performed using a diamond anvil or a belt-type apparatus. Therefore the fact that present results are different from those of Furnish and Bassett [1983] suggests that the type of mechanism is very dependent upon the nature of the stress field of the specimen. Further study will be required to clarify the roll of the stress in detail.

Thermal Expansion

The thermal expansions of α- and γ-Fe$_2$SiO$_4$ at atmospheric pressure and at 5.3 GPa are compared in Figure 5. Data at 5.3 GPa were calculated by the interpolations of several P-V-T data near 5.3 GPa listed in Table 2.

It is remarkable that in γ-Fe$_2$SiO$_4$, thermal expansion is quite different between atmospheric pressure and 5.3 GPa. So far, two measurements have been reported on γ-Fe$_2$SiO$_4$ at atmospheric pressure. Mao et al. [1969] performed X ray powder diffraction up to 400°C and obtained $\alpha = 2.3 \times 10^{-3}$ K^{-1} for the average thermal expansion coefficient between 25°C and 400°C. Yamanaka [1986] performed an X ray single-crystal analysis up to 692°C. His result agreed well with that reported by Mao et al. up to 400°C. Above that temperature, however, Yamanaka observed a rapid increase of the volume. He reported that the single crystal of spinel changed into a polycrystalline state at above 800°C and then transformed into the olivine phase.

The present thermal expansion measurements at high pressure were made only above 500°C in order to avoid complexities caused by the nonhydrostaticity of the pressure. In spinel it is apparent from Figure 5 that at 5.3 GPa volume increases smoothly up to al least 1200°C, and the thermal expansion above 400°C differs considerably between at 5.3 GPa and at atmospheric pressure. In olivine, measurement was made at 1000°C, and thermal expansion at 5.3 GPa is only slightly smaller than that at atmospheric pressure.

Yamanaka reported that when Fe$_2$SiO$_4$ was heated above 400°C, a permanent increase of the lattice parameter was ob-
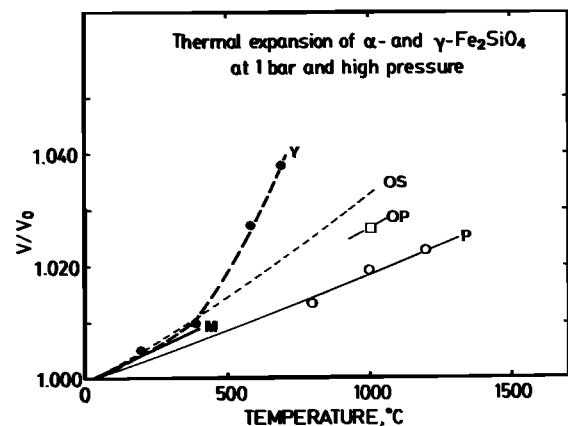

Fig. 5. Thermal expansions of α- and γ-Fe$_2$SiO$_4$ at 1 bar and at 5.3 GPa. OS and OP are for olivine at 1 atm and at 5.3 GPa, respectively. Other lines and circles are for spinel at 1 atm (Y and M) and at 5.3 GPa (P). References are OS, Suzuki et al. [1981]; M, Mao et al. [1969]; Y, Yamanaka [1986]; OP and P, present study.

served after it was cooled to room temperature. This fact suggests that when a quenched crystal is heated above a certain temperature in a metastable condition, partial retrogressive transition occurs within the crystal which can change the apparent volume of the crystal. When the crystal is heated in a stable condition, no such transition occurs, and an intrinsic thermal expansion can be observed. This may be the reason why such a large difference was observed in the thermal expansions of γ-Fe₂SiO₄ between atmospheric pressure and 5.3 GPa.

From the present experiment it is evident that great care should be paid to the use of thermal expansion data of quenched crystals of high-pressure minerals. In order to avoid confusion, reversibility of the volume should be checked when a quenched crystal is heated in a metastable ocndition.

CONCLUSION

Using synchrotron radiation, detailed in situ observations of the olivine-spinel transition in Fe₂SiO₄ were made. It was proved that because of its high brightness and small divergence, synchrotron radiation is a powerful tool to study the behavior of minerals under high pressure and temperature. An accurate phase boundary, density increase associated with the transition at various conditions, and thermal expansion of γ-Fe₂SiO₄ under pressure were determined, and these important parameters are summarized in Table 3.

A comparison between the observed and calculated phase boundary indicate that when the effect of cation disorder is taken into account, the observed phase boundary becomes consistent with thermochemical data for the olivine-spinel transition in Fe₂SiO₄.

It was demonstrated that kinetics of the transition are affected not only by pressure and temperature but also by many other factors. Thus great care should be paid in applying such laboratory experiments to discussions of the earth's interior. Nonuniform formation of the diffraction peaks of spinel phase at the beginning of the transition was not observed in the present study. This fact indicates that the mechanism of the olivine-spinel transition may not be unique, but it may vary with the stress state of the specimen.

The thermal expansion of γ-Fe₂SiO₄ was found to be much smaller than that expected from the high-temperature data obtained at atmospheric pressure. Thermal expansion data of metastable crystals sometimes involve systematic errors caused by the partial progress of the retrogressive transition. In order to make the observation reliable, reversibility of the lattice parameter should be checked carefully.

REFERENCES

Akaogi, M., N. L. Ross, P. McMillan, and A. Navrotsky, The Mg₂SiO₄ polymorphs (olivine, modified spinel, and spinel)— Thermodynamic properties from oxide melt solution calorimetry, phase relations, and models of lattice vibrations, *Am. Mineral.*, *69*, 499–512, 1984.

Akimoto, S., H. Fujisawa, and T. Komada, The olivine-spinel transition in Fe₂SiO₄ and Ni₂SiO₄, *J. Geophys. Res.*, *70*, 1969–1977, 1965.

Akimoto, S., E. Komada, and I. Kushiro, Effect of pressure on the melting of olivine and spinel polymorph of Fe₂SiO₄, *J. Geophys. Res.*, *72*, 679–686, 1967.

Decker, D. L., High-pressure equation of state for NaCl, KCl, and CsCl, *J. Appl. Phys.*, *42*, 3239–3244, 1971.

Furnish, M. D., and W. A. Bassett, Investigation of the mechanism of the olivine-spinel transition in fayalite by synchrotron radiation, *J. Geophys. Res.*, *88*, 10,333–10,341, 1983.

Green, H. W., II, How and why does olivine transform to spinel?, *Geophys. Res. Lett.*, *11*, 817–820, 1984.

Inoue, K., Development of high temperature and high pressure x-ray diffraction apparatus with energy dispersive technique and its geophysical applications, Ph.D. thesis, Tokyo Univ., Tokyo, 1975.

Lauterjung, J., and G. Will, The kinetics of the olivine-spinel transformation in Mg₂GeO₄ under high pressure and temperature, *Physica*, *139/140B*, 343–346, 1986.

Mao, H. K., T. Takahashi, W. A. Bassett, J. S. Weaver, and S. Akimoto, Effect of pressure and temperature on the molar vlumes of wustite and three (Fe, Mg)₂SiO₄ spinel solid solutions, *J. Geophys. Res.*, *74*, 1061–1069, 1969.

Navrotsky, A., Calculation of effect of cation disorder on silicate spinel phase boundaries, *Earth Planet. Sci. Lett.*, *33*, 437–442, 1977.

Navrotsky, A., F. S. Pintchovski, and S. Akimoto, Calorimetric study of the stability of high pressure phases in the systems CoO-SiO₂ and "FeO"-SiO₂, and calculation of phase diagrams in MO-SiO₂ systems, *Phys. Earth Planet. Inter.*, *19*, 275–292, 1979.

Sato, Y., Equation of state of mantle minerals determined through high-pressure x-ray study, in *High Pressure Research: Application to Geophysics*, edited by M. H. Manghnani and S. Akimoto, pp. 307–323, Academic, Orlando, Fla., 1977.

Shimomura, O., S. Yamaoka, T. Yagi, M. Wakatsuki, K. Tsuji, O. Fukunaga, H. Kawamura, K. Aoki, and S. Akimoto, Multianvil type x-ray apparatus for synchrotron radiation, *Mater. Res. Soc. Symp. Proc.*, *22*, 17–20, 1984.

Shimomura, O., S. Yamaoka, T. Yagi, M. Wakatsuki, K. Tsuji, H. Kawamura, N. Hamaya, O, Fukunaga, K. Aoki, and S. Akimoto, Multi-anvil type x-ray system for synchrotron radiation, in *Solid State Physics Under Pressure*, edited by S. Minomura, pp. 351–356, KTK/Reidel, Tokyo, 1985.

Sumino, Y., The elastic constants of Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄, and the elastic properties of olivine group minerals at high temperature, *J. Phys. Earth*, *27*, 209–238, 1979.

Sung, C. M., and R. G. Burns, Kinetics of high-pressure phase transformations: implications to the evolution of the olivine-spinel transition in the downgoing lithosphere and its consequences on the dynamics of the mantle, *Tectonophysics*, *31*, 1–32, 1976.

Suzuki, I., K. Seya, H. Takei, and Y. Sumino, Thermal expansion of fayalite, Fe₂SiO₄, *Phys. Chem. Miner.*, *7*, 60–63, 1981.

Watanabe, H., Thermochemical properties of synthetic high-pressure compounds relevant to the earth's mantle, in *High Pressure Research in Geophysics*, edited by S. Akimoto and M. H. Manghnani, pp. 441–464, Center for Academic Publications Japan, Tokyo, 1982.

Yagi, T., and S. Akimoto, Direct determination of coesite-stishovite transition by in situ x-ray measurements, *Tectonophysics*, *35*, 259–270, 1976.

Yagi, T., F. Marumo, and S. Akimoto, Crystal structure of spinel polymorphs of Fe₂SiO₄ and Ni₂SiO₄, *Am. Mineral.*, *59*, 486–490, 1974.

Yagi, T., Y. Ida, Y. Sato, and S. Akimoto, Effect of hydrostatic pressure on the lattice parameters of Fe₂SiO₄ olivine up to 70 kbar, *Phys. Earth Planet. Inter.*, *10*, 348–354, 1975.

Yagi, T., O. Shimomura, S. Yamaoka, K. Takemura, and S. Akimoto, Precise measurement of compressibility of gold at room and high temperatures, in *Solid State Physics Under Pressure—Recent Advance With Anvil Devices*, edited by S. Minomura, pp. 363–368, KTK/Reidel, Tokyo, 1985.

Yagi, T., M. Akaogi, O. Shimomura, H. Tamai, and S. Akimoto, High pressure and high temperature equations of state of majorite, in *High-Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono, TERRAPUB, Tokyo, in press, 1987.

Yamanaka, T., Crystal structures of Ni₂SiO₄ and Fe₂SiO₄ as a function of temperature and heating duration, *Phys. Chem. Miner.*, *13*, 227–232, 1986.

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