

## The $\text{Mg}_2\text{SiO}_4$ polymorphs (olivine, modified spinel and spinel)—thermodynamic properties from oxide melt solution calorimetry, phase relations, and models of lattice vibrations

MASAKI AKAOGI,<sup>1</sup> NANCY L. ROSS, PAUL MCMILLAN, AND ALEXANDRA NAVROTSKY

*Departments of Chemistry and Geology  
Arizona State University, Tempe, Arizona 85287*

### Abstract

High temperature solution calorimetry of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{Mg}_2\text{SiO}_4$  polymorphs gives  $\Delta H_{1000}^\circ (\alpha \rightarrow \beta) = 7610 \pm 680 \text{ cal mol}^{-1}$  and  $\Delta H_{1000}^\circ (\beta \rightarrow \gamma) = 1630 \pm 900 \text{ cal mol}^{-1}$ . Based on the phase equilibrium data of Suito (1977) and appropriate thermal expansivity, compressibility, and heat capacity data,  $\Delta S_{1000}^\circ = -2.5 \pm 0.5$  and  $-1.5 \pm 0.9 \text{ cal mol}^{-1} \text{ K}^{-1}$  for the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  transitions, respectively. Infrared and Raman spectra have been obtained for the three phases, and the lattice vibrational thermodynamic properties of the  $\text{Mg}_2\text{SiO}_4$  polymorphs have been calculated using the model approach developed by Kieffer (1979c). A range of models consistent with the infrared and Raman data and compressional and shear wave velocities give entropies and heat capacities consistent with reported heat capacities (available only at 350–700 K for  $\beta$ - and  $\gamma$ - $\text{Mg}_2\text{SiO}_4$ ) and with the entropies of transition calculated above. From the vibrational calculations  $\Delta S_{1000}^\circ (\alpha \rightarrow \beta) = -2.8 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$  and  $\Delta S_{1000}^\circ (\beta \rightarrow \gamma) = -1.3 \pm 0.9 \text{ cal mol}^{-1} \text{ K}^{-1}$ . These two approaches to calculating  $\Delta S^\circ$  (calorimetry plus phase equilibria compared to vibrational calculations) offer means of constraining the  $P$ - $T$  slopes of phase transitions at very high pressure, where experimental determinations suffer from serious uncertainties. The thermochemical data for  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{Mg}_2\text{SiO}_4$  are used to construct the  $P, T$  diagram for these phases. The slopes of the  $\alpha$ - $\beta$ -,  $\beta$ - $\gamma$ -, and  $\alpha$ - $\gamma$  boundaries are calculated to be positive and a triple point is predicted to be near 500 ( $\pm 150$ ) K and 120 ( $\pm 10$ ) kbar.

### Introduction

At pressures and temperatures characteristic of the earth's mantle, common silicate minerals transform to denser phases. Thus in the range 130–160 kbar, forsterite ( $\alpha$ - $\text{Mg}_2\text{SiO}_4$  with the olivine structure) transforms first to a modified spinel ( $\beta$ ) and then to a spinel phase ( $\gamma$ ). The detailed study and characterization of such materials is hampered by several problems. The apparatus to reach and control pressures of 100–200 kbar and temperatures of 1000–2000 K is costly to build and operate and generally produces only microgram to milligram quantities of sample. The calibration of pressure and temperature when both are high still has considerable uncertainties. The phases produced may not quench readily to ambient conditions for certain compositions, while for other samples the transformations at high pressure and temperature may be sluggish. Thus although high pressure phase equilibria have been mapped out roughly, the exact location of phase boundaries in  $P, T$  space and the proper reversal of reactions to demonstrate equilibrium remain

largely unattained. Even when high pressure phases can be retained at ambient conditions, they are seldom available in suitable quantity for complete conventional thermodynamic characterization. For example, the measurement of low temperature heat capacity, necessary to calculate the standard entropy of a phase, requires on the order of 1 g or more of sample, making such a study prohibitive for a material synthesized a milligram at a time.

Because of the difficulties and uncertainties described above, it is desirable to constrain the thermodynamic properties of high pressure phases by as many independent lines of evidence as possible. In previous work (Navrotsky, 1973; Navrotsky et al., 1979) we have shown that high temperature solution calorimetry using molten  $2\text{PbO} \cdot \text{B}_2\text{O}_3$  as solvent can measure enthalpies of the olivine–spinel transition in  $\text{Ni}_2\text{SiO}_4$ ,  $\text{Co}_2\text{SiO}_4$ , and  $\text{Fe}_2\text{SiO}_4$  using samples consisting of about 200 mg in total. Such enthalpies can then be used to constrain the pressure–temperature slopes of high pressure phase transitions and offer supporting evidence that the measured phase boundaries in the 30–80 kbar range reasonably approximate equilibrium.

The present work extends these calorimetric studies to

<sup>1</sup> Permanent address: Department of Earth Sciences, Kanazawa University, Kanazawa 920, Japan.

the  $Mg_2SiO_4$  polymorphs. Because of the higher pressure required for their synthesis, these are available in even more limited supply than the corresponding iron, nickel and cobalt silicates, while at the same time their phase relations are more uncertain. The calorimetric data and observed pressures and volume changes of transformation are used to place bounds on the entropy changes and  $P$ - $T$  slopes of the  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  boundaries. At the same time, the entropies of transition are approached using another method, namely modelling of the vibrational contribution to the heat capacity, using newly measured infrared and Raman spectra and the approximations pioneered by Kieffer (1979c). The overall consistency of the entropies obtained using these two approaches (calorimetry plus phase equilibria compared to vibrational models) puts tighter constraints on values of  $\Delta S^\circ$  for the transitions than does either approach alone and suggests that such vibrational calculations may be useful for phases about which we have even less reliable thermodynamic information, e.g., the post-spinel phases in the system  $MgO$ - $SiO_2$ ,  $MgSiO_3$  ilmenite and perovskite.

## Experimental procedure

### Sample synthesis and characterization

$Mg_2SiO_4$  olivine (about 5 g) was synthesized from an intimate mixture of  $MgO$  and silicic acid heated at 1573 K for 112 hr. Powder X-ray diffraction, microscopic observation and its Raman and infrared spectra indicated that the synthesized sample was single phase  $\alpha$ - $Mg_2SiO_4$ .

A reactive forsterite was used as a starting material for synthesis of  $\beta$ - $Mg_2SiO_4$  because the transition of well crystallized forsterite to  $\beta$ -phase is sluggish. A gel with  $Mg/Si = 2$  was precipitated by mixing an alcoholic solution of ethyl orthosilicate and an aqueous solution of magnesium nitrate. The precipitated gel was heated at 1123 K for 127 hr. Powder X-ray diffraction data of the sample thus prepared showed the presence of very fine grained forsterite ( $\sim 80\%$ ) and unreacted periclase plus silica ( $\sim 20\%$ ). The stoichiometric  $Mg/Si$  ratio of 2 of this starting material was confirmed by electron microprobe analysis of the forsterite sintered at high pressure and high temperature from this starting material. High-pressure high-temperature syntheses were made using a double-stage, cubic-octahedral-anvil apparatus in the University of Tokyo, Japan. The starting material was put directly into a platinum cylindrical furnace, and was held at 145 kbar and 1123 K for 1 hr. The quenched sample was examined by powder X-ray diffraction and microscopic observation. It was well crystallized  $\beta$ - $Mg_2SiO_4$  ( $\sim 200$  mg) with very small amounts of forsterite ( $<1\%$ ) and platinum ( $\sim 0.1\%$ ).

The  $\gamma$ -phase used in this work was kindly provided by Dr. E. Ito. For synthesis of the  $\gamma$ - $Mg_2SiO_4$ , a uniaxial split-sphere type high-pressure apparatus in Okayama University, Misasa, Japan, was used. The starting material (forsterite) was put into a cylindrical platinum heater and was held at 220 kbar and 1473 K for 1 hr. The sample was quenched and examined by powder X-ray diffraction and microscopic observation. The product ( $\sim 30$  mg) was well crystallized  $\gamma$ - $Mg_2SiO_4$  with a small amount ( $<2\%$  total) of  $MgSiO_3$  perovskite and periclase.

### Calorimetry

High-temperature solution calorimetric techniques in this study were the same as those described previously (Navrotsky, 1977). A twin Calvet-type microcalorimeter was used to measure enthalpies of solution of three polymorphs of  $Mg_2SiO_4$  in molten  $2PbO \cdot B_2O_3$  at 975 K. For the calorimetry of  $\alpha$ - $Mg_2SiO_4$ , incomplete dissolution was a problem in the initial runs using a solid-bottomed sample cup. Therefore sample containers with perforated platinum foil bottoms described by Navrotsky et al. (1980) were used. A thin platinum foil bottom, perforated with about 50 holes of diameters less than  $80 \mu m$ , was attached to the platinum sample holder to form a miniature colander. The grains of  $\alpha$ - $Mg_2SiO_4$  were sized not to pass through the holes. By using this cup with several rapid stirrings during the first few minutes, the  $\alpha$ - $Mg_2SiO_4$  was dissolved rapidly and completely.

Metastability of  $\beta$ - $Mg_2SiO_4$  and  $\gamma$ - $Mg_2SiO_4$  in the calorimeter at 975 K was examined after equilibration for 5 hours. Both powder X-ray diffraction and microscopic observation indicated no evidence of back-transformation in the  $\beta$ -phase. However, the powder X-ray diffraction pattern of the heated  $\gamma$ - $Mg_2SiO_4$  showed weak reflections of  $\alpha$ - $Mg_2SiO_4$  together with strong peaks of the  $\gamma$ -phase suggesting the beginning of back-transformation. Microscopic observation revealed a relatively small amount of highly birefringent material with refractive index lower than 1.68 plus a large amount of isotropic material with refractive index of  $1.703 \pm 0.006$ . The optical properties of both phases clearly indicated that the former was  $\alpha$ - $Mg_2SiO_4$ , while the latter was  $\gamma$ - $Mg_2SiO_4$ . The amount of  $\alpha$ - $Mg_2SiO_4$  in the heated  $\gamma$ -phase was estimated to be  $10 \pm 5\%$  from its volume by microscopic observation. To minimize any effect of this back-transformation on the heats of solution, the equilibration time of the  $\gamma$ - $Mg_2SiO_4$  in the calorimeter prior to the solution run was reduced to 3 hours, and the observed heat of solution of the  $\gamma$ -phase was corrected for the  $10\%$   $\alpha$ - $Mg_2SiO_4$  present in the sample (see Table 1). Although no back-transformation of  $\beta$ - $Mg_2SiO_4$  was observed, the time of equilibration was also reduced to 3-5 hours. Both  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  were dissolved rapidly and completely in the flux. As described previously, the  $\beta$ -phase and  $\gamma$ -phase contained small amounts of phases other than the  $Mg_2SiO_4$  polymorphs ( $<1\%$  and  $<2\%$ , respectively). No correction was made for these because their amounts were small and the heat of solution of  $MgSiO_3$  perovskite is unknown.

### Infrared and Raman spectroscopy

Near infrared powder transmission spectra were run in KBr discs between 300 and  $1400 \text{ cm}^{-1}$  using a Nicolet MX-1 interferometer. The amount of sample in each disc was 3.0 mg for 250 mg KBr. Far-infrared spectra were obtained with a Perkin-Elmer 180 spectrophotometer in the laboratory of Dr. George Rossman at the California Institute of Technology. Small amounts of specimen powder (2.0-3.0 mg) were mixed with Vaseline petroleum jelly on polyethylene plates. Scanning speed was variable, generally from 5 to  $10 \text{ cm}^{-1}/\text{min}$  and the slit width was also variable. Raman spectra were obtained by glancing angle reflection from a wall or pellet of powdered sample, using the 4880 or  $5145 \text{ \AA}$  line of a Spectra-Physics 171 argon laser, and a Spex 1402 double monochromator equipped with an RCA photomultiplier and photon-counting electronics. Laser power at the sample was 100-200 mW for the high-pressure phases to avoid overheating the samples. Slit widths were near  $2 \text{ cm}^{-1}$ .

Table 1. Enthalpies of solution of Mg<sub>2</sub>SiO<sub>4</sub> polymorphs in 2PbO · B<sub>2</sub>O<sub>3</sub> at 975 K

Sample weight (mg)	ΔH <sub>sol</sub> <sup>o</sup> (cal mol <sup>-1</sup> )
<b>α-Mg<sub>2</sub>SiO<sub>4</sub></b>	
31.19	15447
25.90	15263
26.08	16406
22.23	15867
24.40	16617
15.11	16815
17.28	16074
18.52	15865
Average	16044 (8) s(data) = 546 <sup>a</sup> s(mean) = 193
<b>β-Mg<sub>2</sub>SiO<sub>4</sub></b>	
15.99	8496
14.92	9201
14.49	8488
15.35	8590
13.69	9111
13.83	9397
Average	8881 (6) s(data) = 402 s(mean) = 164
<b>γ-Mg<sub>2</sub>SiO<sub>4</sub></b>	
14.82	8554
7.73	7705
Average	8130 ± 425 (2) s(data) = 425
Average (corrected for 10% α)	7251 ± 700

<sup>a</sup> number in parentheses is number of runs, s(data) is standard deviation of the data, s(mean) is standard deviation of the mean. 1 cal = 4.184 joule.

## Thermochemical results and discussion

### Calorimetric data

Enthalpies of solution of the olivine, modified spinel and spinel phase of Mg<sub>2</sub>SiO<sub>4</sub> are shown in Table 1. Note that throughout this paper, calories are used; 1 cal = 4.184 joule. To calculate the enthalpy of solution of pure γ-Mg<sub>2</sub>SiO<sub>4</sub>, the observed enthalpy of solution was corrected for the presence of 10% olivine. The heat of solution of α-Mg<sub>2</sub>SiO<sub>4</sub> shown in Table 1 is consistent with values measured by Charlu et al. (1975) and Wood and Kleppa (1981) within experimental error. Using the data in Table 1, the standard enthalpies at 975 K for the transitions among α-, β- and γ-Mg<sub>2</sub>SiO<sub>4</sub> were calculated and are shown in Table 2 together with the data for the α-β-γ transitions in Co<sub>2</sub>SiO<sub>4</sub> obtained previously (Navrotsky et al., 1979). Table 2 also contains the volume changes at 298 K and the calculated entropy changes, which will be discussed below in detail.

Note that the runs on β-Mg<sub>2</sub>SiO<sub>4</sub> and on γ-Mg<sub>2</sub>SiO<sub>4</sub> used totals of 88 and 23 mg, respectively, and that each run generally used about 15 mg. The results show a standard deviation of the data of about 400 cal, or a

standard deviation of the mean of less than 200 cal. Thus reliable enthalpy of solution data can be obtained using the small amounts of sample available through high pressure synthesis.

### Calculation of phase relations

From the enthalpy changes in Table 2, we can calculate slopes of the phase boundaries based on the Clausius-Clapeyron relation. To locate the phase boundaries in *P-T* space, the standard free energy of the transition at atmospheric pressure or the equilibrium transition pressure at the same temperature is required. For accurate calculations of the *P-T* slopes of the phase boundaries, the effects of compression and thermal expansion must be included. In the previous paper (Navrotsky et al., 1979), the phase boundaries were calculated including the effect of compression and thermal expansion but using the approximation of constant standard enthalpy and entropy changes for the transitions. In this work we adopt a better approximation in which the temperature dependence of enthalpy and entropy of transition is included by using the heat capacity data recently reported by Watanabe (1982). First, the effect of compression at a desired pressure and 298 K is calculated using a Murnaghan equation. Next, using X-ray and dilatometric data obtained at high temperature and one atmosphere, the molar volume is fitted as a linear function of temperature (a good fit between 300 and 1200 K and a reasonably reliable extrapolation to higher temperature). This results in the equation,

$$V_{T,P} = [V_{298}^3 + a'(T - 298)] \cdot [PK'/K + 1]^{-1/K'} \quad (1)$$

in which  $V_{298}^3$  is the molar volume at 298 K and 1 atm,  $a'$  is a constant related to the thermal expansion coefficient,  $K$  and  $K'$  are the bulk modulus and its pressure derivative respectively,  $P$  is the pressure in kbar and  $T$  is the absolute temperature. This formalism approximates the effects of pressure and temperature as separate contributions. As discussed previously (Navrotsky et al., 1979)

Table 2. Thermochemical data for phase transitions among Mg<sub>2</sub>SiO<sub>4</sub> and Co<sub>2</sub>SiO<sub>4</sub> polymorphs

Compound	ΔV <sub>298</sub> <sup>o</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	ΔH <sub>1000</sub> <sup>o</sup> (cal mol <sup>-1</sup> )	ΔS <sub>1000</sub> <sup>o</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )
Mg <sub>2</sub> SiO <sub>4</sub> , α+β	-3.13 <sup>a</sup>	7160 ± 680 <sup>a</sup>	-2.5 ± 0.5 <sup>a</sup> , -2.8 ± 0.6 <sup>c</sup>
Co <sub>2</sub> SiO <sub>4</sub> , <sup>b</sup>	-2.90 <sup>b</sup>	2150 ± 390 <sup>b</sup>	-2.16 ± 0.3 <sup>b</sup>
Mg <sub>2</sub> SiO <sub>4</sub> , β+γ	-0.89 <sup>a</sup>	1630 ± 900 <sup>a</sup>	-1.5 ± 0.9 <sup>a</sup> , -1.3 ± 0.9 <sup>c</sup>
Co <sub>2</sub> SiO <sub>4</sub> , <sup>b</sup>	-1.02 <sup>b</sup>	540 ± 430 <sup>b</sup>	-0.98 ± 0.3
Mg <sub>2</sub> SiO <sub>4</sub> , α+γ	-4.02 <sup>a</sup>	8790 ± 890 <sup>a</sup>	-4.0 ± 0.7 <sup>a</sup> , -4.1 ± 1.0 <sup>c</sup>
Co <sub>2</sub> SiO <sub>4</sub> , <sup>b</sup>	-3.92 <sup>b</sup>	2690 ± 300 <sup>b</sup>	-3.14 ± 0.3 <sup>b</sup>

<sup>a</sup>this work, based on calorimetry and phase equilibria. 1 cal = 4.184 joule.  
<sup>b</sup>Navrotsky et al. (1979).  
<sup>c</sup>this work, based on vibrational calculations.

Table 3. Parameters used in phase diagram calculations

Compound	$V_{998}^0$ ( $cm^3 mol^{-1}$ )	$a'$ ( $cm^3 mol^{-1} K^{-1}$ )	$K_0$ (kbar)	$K_0'$	$C_p = a + bT + cT^{-2}$ ( $cal mol^{-1} K^{-1}$ ) <sup>j</sup>		
					a	$b \times 10^3$	$c \times 10^{-5}$
$\alpha$ - $Mg_2SiO_4$	43.67 <sup>a</sup>	0.00162 <sup>d,k</sup>	1290 <sup>g</sup>	5.2 <sup>g</sup>	37.25	5.313	-9.786
$\beta$ - $Mg_2SiO_4$	40.54 <sup>a,b</sup>	0.00128 <sup>e,k</sup>	1660 <sup>h</sup>	4 <sup>i</sup>	36.29	5.519	-10.309
$\gamma$ - $Mg_2SiO_4$	39.65 <sup>a,c</sup>	0.00104 <sup>f,k</sup>	2130 <sup>h</sup>	4 <sup>i</sup>	37.41	3.457	-11.436

a. Jeanloz and Thompson (1983), b. Akimoto et al. (1976), c. Ito et al. (1974), d. Hazen (1976), Smyth and Hazen (1973), Suzuki (1979), e. Suzuki et al. (1980), f. Suzuki et al. (1975), g. Graham and Barsch (1969), Kumazawa and Anderson (1969), h. Mizukami et al. (1975), i. Assumed, j. Watanabe (1982) (1 cal = 4.184 joule, k. calculated by fitting straight line to molar volume as function of temperature (T in K) using indicated data, see text.

this relatively crude approximation is useful when more complete data on thermal expansion and compressibility at various  $T$  and  $P$  are lacking, as for  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$ . Using the heat capacities, changes of enthalpy and entropy for the transition with temperature are calculated by the following equations

$$\Delta H_T^0 = \Delta H_{T_0}^0 + \int_{T_0}^T \Delta C_P dT \quad (2)$$

$$\Delta S_T^0 = \Delta S_{T_0}^0 + \int_{T_0}^T \frac{\Delta C_P}{T} dT \quad (3)$$

where  $\Delta H_T^0$  and  $\Delta S_T^0$  are the enthalpy and entropy of transition, respectively at temperature  $T$  and atmospheric pressure,  $T_0$  is the temperature of calorimetry, and  $\Delta C_P$  is the heat capacity difference at  $T$  and 1 atm. The standard free energy of transition is then given by

$$\Delta G_T = \Delta H_T^0 - T\Delta S_T^0 + \int_{1 \text{ atm}}^P \Delta V_{T,P} dP \quad (4)$$

in which  $\Delta V_{T,P}$  is the volume change for the transition calculated from equation (1). At equilibrium along the phase boundary

$$\Delta G_T = 0 \quad (5)$$

Therefore, by using  $\Delta H_{975}^0$  and one  $P, T$  point on the phase boundary, together with  $V^0(T)$ ,  $K$ ,  $K'$  and  $C_P$  of the phases involved, we can calculate the phase boundary in the  $P$ - $T$  space and also examine the sensitivity of the calculated boundary to the parameters. The parameters used in the calculations are listed in Table 3.

Two significantly different versions of the high pressure relations among  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $Mg_2SiO_4$  have been presented by Suito (1977) and by Kawada (1977). As shown in Figure 1, the transition pressure of Suito's boundary for the  $\alpha$ - $\beta$  transition, [ $P$  (kbar) = 98 + 0.035  $T$  (K)] is ~15–20 kbar higher than that of Kawada's boundary, [ $P$  (kbar) = 43 + 0.068  $T$  (K)]. Also the slope of Kawada's  $\alpha$ - $\beta$  boundary is about two times larger than Suito's. When Suito's transition pressure at 975 K is used with the enthalpy of  $\alpha$ - $\beta$  transition in Table 2, the calculated slope (0.027 kbar  $K^{-1}$ ) is rather consistent with Suito's slope. However, if Kawada's transition pressure at 975 K is used, the calculated slope (0.003 kbar  $K^{-1}$ ) is inconsistent with Kawada's value. To compare the calculated boundary with Suito's experimental results in more detail, the results of runs by Suito (1977) and the calculated phase boundaries from the thermochemical data are shown in Figure 2. In the calculation of the calorimetric phase boundaries, the transition point of 143 kbar and 1273 K on Suito's boundary was chosen, because, at that temperature, reaction rates probably would be fast enough for the observed transition pressure to approximate the equilibrium pressure. Suito's data permit a range of slope for the boundary. Calculated phase boundaries with three different slopes in the allowable range, consistent with the uncertainty in the calorimetric enthalpy of transition, are

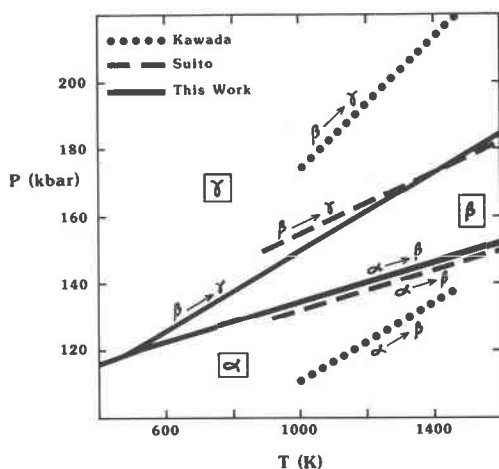


Fig. 1. Pressure-temperature relations for the  $Mg_2SiO_4$  polymorphs. Solid lines are this work, parameters in Tables 2 and 3, discussion in text. Dotted and dashed boundaries are from Kawada (1977) and Suito (1977) respectively.

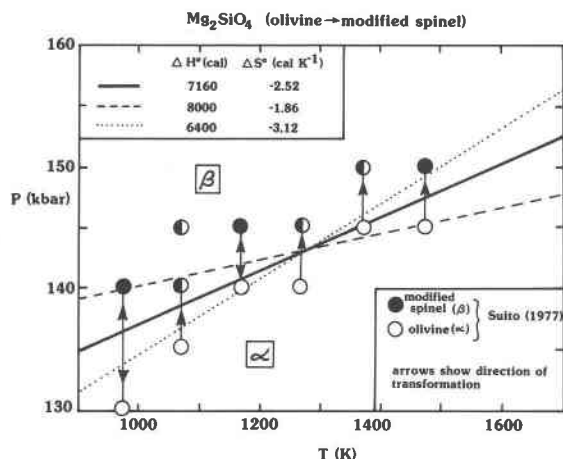


Fig. 2. Calculated phase boundary for  $\alpha \rightarrow \beta$   $Mg_2SiO_4$  transition compared to experimental data (points) of Suito (1977). Solid line indicates best estimate of thermochemical parameters (calculations described in text), dashed and dotted lines represent extreme values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  allowed by calorimetric data and  $(P, T)$  point at 1273 K.

shown in Figure 2. The calculated values of  $\Delta S^\circ_{1000}$  corresponding to these three boundaries are also shown in the figure. Figure 2 shows that the thermochemical data for the  $\alpha$ - $\beta$  transition in  $Mg_2SiO_4$  ( $\Delta H^\circ_{1000} = 7160 \pm 680$  cal/mol,  $\Delta S^\circ_{1000} = -2.5 \pm 0.5$  cal mol $^{-1}$  K $^{-1}$ ), listed in Table 2, completely satisfy Suito's experimental results.

One may consider the sources of the discrepancy in the  $\alpha$ - $\beta$  boundary between the data of Suito (1977) and of Kawada (1977). A probable cause is the difference of pressure calibration at high temperatures, which is related to differences in the high-pressure apparatus used in their studies. Using the coesite-stishovite boundary of Yagi and Akimoto (1976), Suito found virtually no difference between pressures at 90–100 kbar and 873–1473 K, and those calibrated at room temperature in his experiments using a uniaxial split-sphere high-pressure apparatus. However, in Kawada's work, using a Bridgman-anvil apparatus, a large pressure correction was inferred from calibration near 1273 K and 90–100 kbar. Uncertainties in this correction may be large enough to account for the differences in both absolute values of pressure and in  $P$ - $T$  slopes. As shown in Figure 1, thermochemical data obtained in this study are quite consistent with Suito's results, but not with Kawada's.

Very recently, Fukizawa (1982) determined the  $\alpha$ - $\beta$  transition pressure in  $Mg_2SiO_4$  by means of high-pressure high-temperature experiments using an in-situ X-ray diffraction method, in which pressure values were measured based on a gold pressure standard. Although his data are still preliminary, a combination of the enthalpy of transition obtained in our work with an accurately determined  $P, T$  point, based on in-situ X-ray diffraction experiments at high pressures and high temperatures, would provide further refinement of the phase boundary.

It is somewhat difficult to locate accurately the  $\beta$ - $\gamma$  phase boundary calculated from the thermochemical data. In the  $\beta$ - $\gamma$  transition, since  $\Delta H^\circ$  and  $\Delta S^\circ$  are small, the  $\int_{1}^P \Delta V_{T,P} dP$  term in equation (4) is of comparable magnitude to  $\Delta H^\circ$  and  $T\Delta S^\circ$ . Therefore, the errors in compressibilities, thermal expansivities and heat capacities of  $\beta$ - and  $\gamma$ -phase result in great uncertainties in  $\Delta G(P, T)$ . Furthermore, considerably different lattice parameters for  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  than those used in Tables 2 and 3 have been recently reported (Horiuchi and Sawamoto, 1981; Sasaki et al., 1982). The new cell volumes of  $\beta$ - and  $\gamma$ -phase result in a volume change  $\Delta V_{298}^\circ$  ( $\beta \rightarrow \gamma$ ), of  $-1.02$  cm $^3$  mol $^{-1}$ , which is about 15% larger in magnitude than the  $-0.89$  cm $^3$  mol $^{-1}$ , listed in Table 2 and 3. In addition, the thermal expansion data of Suzuki et al. (1980) show considerable scatter and Sato (1970) suggested that the thermal expansivity of  $\beta$ - $Co_2SiO_4$  is smaller than that of  $\gamma$ - $Co_2SiO_4$ . Thus considerable uncertainty exists in the value of  $\Delta V$  ( $\beta \rightarrow \gamma$ ). The solid line (curve 1) in Figure 3 is calculated with  $\Delta H = 1630$  cal mol $^{-1}$ ,  $\Delta S = -1.5$  cal mol $^{-1}$  K $^{-1}$  and  $\Delta V = -0.89$  cm $^3$  mol $^{-1}$ , independent of  $P$  and  $T$  (as in Table 2). The points represent the phase transformation data of Suito (1977). Note that none of these points has been reversed so that they may represent synthesis rather than equilibrium

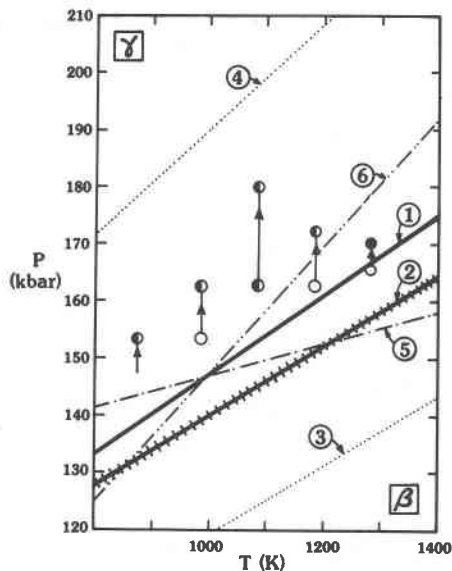


Fig. 3. The  $\beta$ - $\gamma$  transition. Points represent experiments of Suito (1977). Solid line, curve 1, is "best" thermochemical calculation, with  $\Delta H^\circ = 1630$  cal mol $^{-1}$ ,  $\Delta S^\circ = -1.5$  cal mol $^{-1}$  K $^{-1}$ ,  $\Delta V^\circ = -0.89$  cm $^3$  mol $^{-1}$ . Hatched line (curve 2) is experimental phase boundary quoted by Sawamoto (1983, personal communication). Other lines are calculated using values of  $\Delta H^\circ$  (cal mol $^{-1}$ ),  $\Delta S^\circ$  (cal mol $^{-1}$  K $^{-1}$ ),  $\Delta V^\circ$  (cm $^3$  mol $^{-1}$ ) allowed by uncertainties in experimental data as follows: curve 3,  $\Delta H^\circ = 1630$ ,  $\Delta S^\circ = -1.5$ ,  $\Delta V^\circ = -1.09$ ; curve 4,  $\Delta H^\circ = 1630$ ,  $\Delta S^\circ = -1.5$ ,  $\Delta V^\circ = -0.69$ ; curve 5,  $\Delta H^\circ = 2530$ ,  $\Delta S^\circ = -0.6$ ,  $\Delta V^\circ = -0.89$ ; curve 6,  $\Delta H^\circ = 730$ ,  $\Delta S^\circ = -2.4$ ,  $\Delta V^\circ = -0.89$ .

conditions. Indeed a  $\beta$ - $\gamma$  boundary at somewhat lower pressures, shown by curve 2 in Figure 3, has been suggested from crystal growth experiments by Sawamoto (1983, pers. comm.). The calculated curve lies between these two determinations.

The lower and upper dotted lines (curves 3 and 4) show the effect of changing  $\Delta V$  by  $\pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$  while keeping  $\Delta H^\circ$  and  $\Delta S^\circ$  constant. The dot-dashed and double-dot-dashed lines (curves 5 and 6) show the effect of varying  $\Delta H^\circ$  by the calorimetric uncertainty and adjusting  $\Delta S^\circ$  to keep  $\Delta G_{1000}^\circ$  constant, while keeping  $\Delta V^\circ = -0.89 \text{ cm}^3 \text{ mol}^{-1}$ . Numerous other boundaries, generally falling between curves 3 and 4, can be generated by simultaneous variation of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta V^\circ$  within limits consistent with the uncertainties in the calorimetric, X-ray, and phase boundary data. (Note that to maintain such consistency, variations, in  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta V^\circ$  can not be made completely independently of each other.) We conclude that the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta V^\circ$  listed for the  $\beta \rightarrow \gamma$  transition in Table 2 are consistent with the phase relations and thermochemical data as currently known, but tighter constraints on these parameters must await further study, including that of thermal expansion and compressibility.

Figure 1 summarizes the calorimetric boundaries of  $\alpha$ - $\beta$ - $\gamma$  transitions in  $Mg_2SiO_4$ . The  $\alpha$ - $\gamma$  boundary was calculated from the data in Table 2. The calorimetric boundaries define a triple point at approximately 120 kbar and 500 K. The uncertainties in this value arising from uncertainties in the calculated  $P, T$  boundaries are of the order of  $\pm 150 \text{ K}$  and  $\pm 10 \text{ kbar}$ . The phase boundaries determined from the high pressure studies of Suito (1977) and Kawada (1977) also suggest a triple point, probably at somewhat lower temperature than that calculated from the thermochemical data.

### Relation of thermochemical and structural parameters

$\Delta V^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the  $\alpha$ - $\beta$  transition in  $Mg_2SiO_4$  are 78, 81, and 63%, respectively, of the corresponding values for the  $\alpha$ - $\gamma$  transition. In the previous calorimetric study on the high-pressure polymorphs of  $Co_2SiO_4$  (Navrotsky et al., 1979), quite similar results were obtained:  $\Delta V_{298}^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the  $\alpha$ - $\beta$  transition in  $Co_2SiO_4$  are 74, 80 and 69%, respectively, of those for the  $\alpha$ - $\gamma$  transition. These results suggest that, on the basis of thermochemical properties, the  $\beta$ -phase resembles the spinel rather than olivine. The  $\alpha$ - $\beta$ - $\gamma$  transition do not involve any changes in the coordination numbers of cations. However, the structures of  $\beta$ -phase and spinel are based on a slightly distorted cubic close packing of oxygen atoms, while the olivine structure is based on hexagonal close packing. Recent structural studies on  $\beta$ - $Mg_2SiO_4$  and  $\gamma$ - $Mg_2SiO_4$  reveal that a small increase of mean Si-O bond length and a decrease of average Mg-O distance are observed in the  $\alpha \rightarrow \beta \rightarrow \gamma$  transitions, and that

these changes are larger in the  $\alpha \rightarrow \beta$  transition than in the  $\beta \rightarrow \gamma$  transition (Horiuchi and Sawamoto, 1981; Sasaki et al., 1982). Similar results were obtained for the  $\alpha \rightarrow \beta \rightarrow \gamma$  transitions in  $Co_2SiO_4$  (Morimoto et al., 1974). Therefore, in terms of structural data, as well in terms of the thermochemical data presented here, the  $\beta$ -phase is more similar to spinel than to olivine for both  $Mg_2SiO_4$  and  $Co_2SiO_4$ .

### Vibrational spectra, models of lattice vibrations, and calculation of vibrational entropies

#### Vibrational spectra

The observed near- and far-infrared and Raman spectra for  $\alpha$ -,  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  are shown in Figure 4 and the peaks are tabulated in Table 4. The infrared and Raman spectra for  $\alpha$ - $Mg_2SiO_4$  (forsterite) are comparable to those of previous workers (Oehler and Gunthard, 1969; Servoin and Piriou, 1973; Iishi, 1978). Factor group analysis (e.g., Fateley et al., 1972) gives the number and symmetries of expected bands, summarized below for the three phases.

- (a)  $\alpha$ - $Mg_2SiO_4$ : Space group  $Pbnm$ :  $Z = 4$   
 Raman:  $11 A_g + 7 B_{1g} + 11 B_{2g} + 7 B_{3g}$   
 Infrared:  $14 B_{1u} + 10 B_{2u} + 14 B_{3u}$   
 Inactive:  $10 A_u$   
 Acoustic:  $B_{1u} + B_{2u} + B_{3u}$
- (b)  $\beta$ - $Mg_2SiO_4$ : Space group  $Imma$ :  $Z = 4$  (for primitive cell)  
 Raman:  $11 A_g + 7 B_{1g} + 9 B_{2g} + 12 B_{3g}$   
 Infrared:  $14 B_{1u} + 13 B_{2u} + 11 B_{3u}$   
 Inactive:  $7 A_u$   
 Acoustic:  $B_{1u} + B_{2u} + B_{3u}$
- (c)  $\gamma$ - $Mg_2SiO_4$ : Space group  $Fd3m$ :  $Z = 2$  (for primitive cell)  
 Raman:  $A_{1g} + E_g + 3F_{2g}$   
 Infrared:  $4 F_{1u}$   
 Inactive:  $F_{1g} + 2 A_{2u} + 2 E_u + 2 F_{2u}$   
 Acoustic:  $F_{1u}$

The infrared spectrum of  $\gamma$ - $Mg_2SiO_4$  shows a major band near  $830 \text{ cm}^{-1}$ , comparable to those for  $\gamma$ - $Fe_2SiO_4$ ,  $\gamma$ - $Ni_2SiO_4$  and  $\gamma$ - $Co_2SiO_4$  (Jeanloz, 1980). These last three phases also show distinct bands near 500 and  $350 \text{ cm}^{-1}$ , while the  $\gamma$ - $Mg_2SiO_4$  sample has only a single broad band centered near  $445 \text{ cm}^{-1}$  (Fig. 4), which may contain components corresponding to the two bands of the Fe-, Ni- and Co- phases. Assignment of these bands has been discussed by Jeanloz (1980). The  $830 \text{ cm}^{-1}$  band has marked shoulders near  $930$  and  $790 \text{ cm}^{-1}$ , while the  $445 \text{ cm}^{-1}$  band shows shoulders near  $510$  and  $395 \text{ cm}^{-1}$ , and two weak sharp features at  $543$  and  $348 \text{ cm}^{-1}$ . The  $510 \text{ cm}^{-1}$  shoulder may correspond to the band near  $500 \text{ cm}^{-1}$  observed for the Fe-, Ni- and Co- spinels by Jeanloz (1980). However, only four infrared bands are expected for  $\gamma$ - $Mg_2SiO_4$ . The additional features could be due to some deviation of the spinel from cubic symmetry but none was indicated by the X-ray study of Sasaki et al.

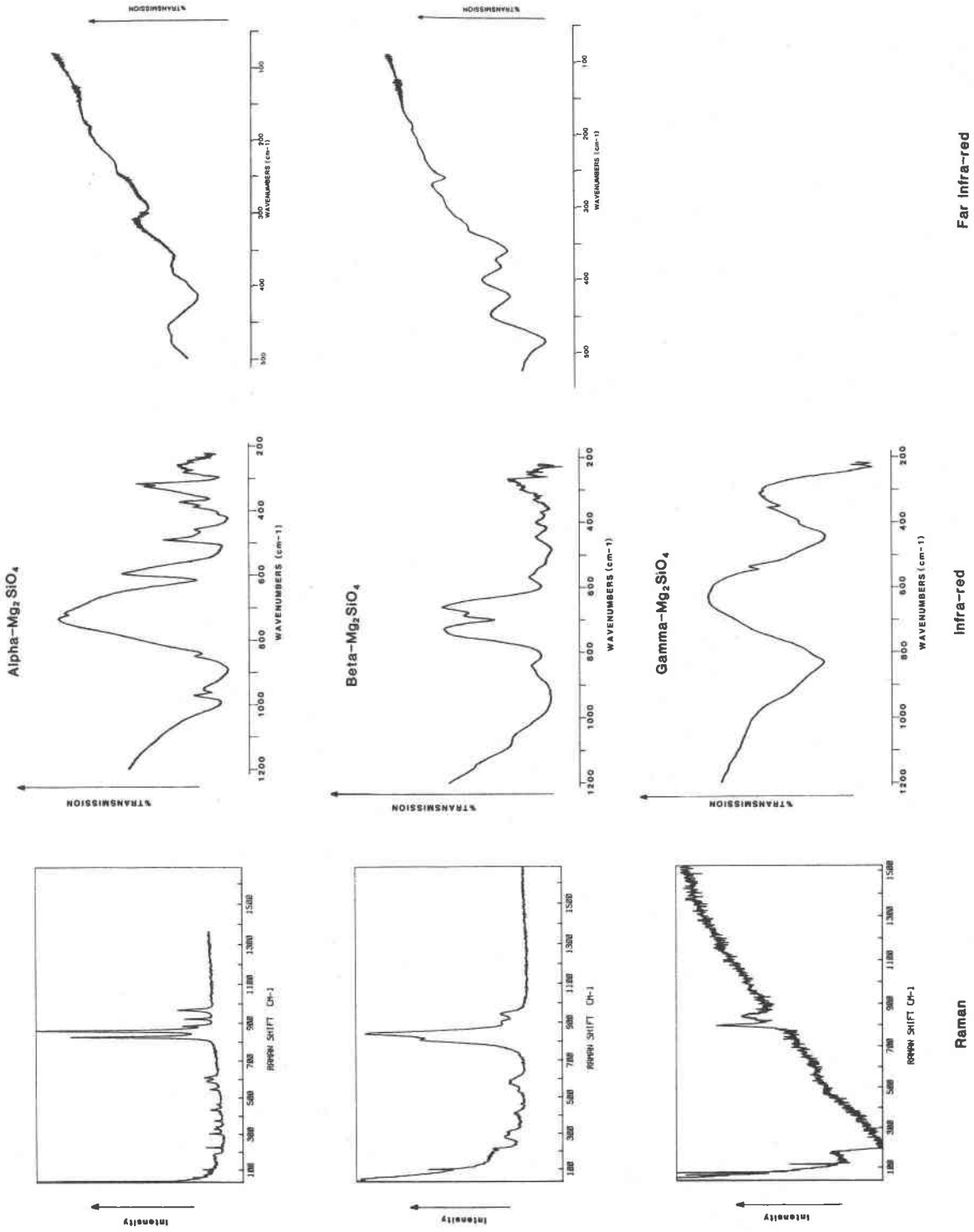


Fig. 4. Infrared and Raman spectra of  $\alpha$ -,  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$ .

Table 4. Observed infrared and Raman bands for  $\alpha$ -,  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$ 

		$\alpha$ - $Mg_2SiO_4$		$\beta$ - $Mg_2SiO_4$		$\gamma$ - $Mg_2SiO_4$	
Raman		Infrared		Raman	Infrared	Raman	Infrared
163	$B_{1g}$	135 ?	$B_{2u}$		130 ?		
180	$A_g$	184	$B_{1u}+B_{3u}$	213	188		
223	$A_g$	228	$B_{1u}+B_{2u}+B_{3u}$		208		
300	$A_g$	268 sh	$B_{1u}+B_{3u}$		226		
312	$B_{1g}+B_{3g}$	293	$B_{1u}+B_{2u}+B_{3u}$				
		318 ?	$B_{3u}$	280	288		
325	$B_{2g}+A_g$			307	316 ?sh		
336	$A_g$	336 sh	$B_{3u}$		326		
		360	$B_{1u}+B_{2u}$				
371	$B_{2g}+B_{3g}$	378 sh	$B_{3u}$		345 sh		350 w
					359		
		395 sh	$B_{2u}+B_{3u}$		381		
		416	$B_{1u}+B_{2u}$	408			395 sh
430	$A_g+B_{1g}$			460	422	455	445
438	$B_{2g}$				485		510 sh
460	$B_{3g}$	470	$B_{1u}$ or $B_{2u}$	528	520	550	545 w
		480 sh	$B_{1u}$		550		
		510	$B_{1u}+B_{2u}$	570	595		
542	$A_g$	540 sh	$B_{2u}$	588	645 sh		
					675		
586	$B_{1g}+B_{2g}+B_{3g}$	570 sh	$B_{3u}$		700		
606	$A_g$	615	$B_{3u}$	850 $A_g?$	805	781 $A_g?$	785 sh
820	$A_g$	840	$B_{2u}+B_{3u}$	836 $A_g?$			830
853	$A_g$				855		
878	$B_{2g}$	870 sh	$B_{1u}+B_{2u}+B_{3u}$	898		877 $F_{2g}?$	920 sh
		890		919	910		
916	$B_{3g}$			940	945		
					985 sh		
962	$A_g$	960	$B_{3u}$		1080 sh		
					1150 sh		
		990	$B_{2u}+B_{3u}$				

Notes: All frequencies are in  $cm^{-1}$ . Infrared positions were estimated at the transmission minima. Band symmetry assignments for  $\alpha$ - $Mg_2SiO_4$  are from Servoin and Piriou (1973) and Iishi (1978). Suggested assignments for  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  are from band intensities. The queried (?) bands at 135 and 130  $cm^{-1}$  in the far infrared spectra of  $\alpha$ - and  $\beta$ - $Mg_2SiO_4$  occur in a noisy part of the spectrum, but may be real. A band was observed at 144  $cm^{-1}$  for  $\alpha$ - $Mg_2SiO_4$  by Oehler and Gunthard (1969), and appeared in the calculation of Iishi (1978). Sh means shoulder, w means weak.

(1982), although some Mg-Si disorder was possible. Jeanloz (1980) observed similar shoulders on the major bands of  $\gamma$ - $Fe_2SiO_4$ ,  $\gamma$ - $Ni_2SiO_4$  and  $\gamma$ - $Co_2SiO_4$ , which he attributed to some vibrational coupling between octahedral and tetrahedral cation site vibrations. No far-infrared spectrum was obtained for the  $\gamma$ - $Mg_2SiO_4$  sample, but studies of other silicate spinels suggest a further band below 400  $cm^{-1}$  (White and DeAngelis, 1967). The Raman spectrum of  $\gamma$ - $Mg_2SiO_4$  (Fig. 4) shows two major bands at 781 and 877  $cm^{-1}$ . These are probably respectively the  $A_{1g}$  and  $F_{2g}$  modes derived from  $\nu_1$  (symmetric) and  $\nu_3$  (asymmetric) stretching motions of the tetrahedral  $SiO_4$  groups (see White, 1975; Piriou and McMillan, 1983). These are at lower frequency than the corresponding bands in  $\alpha$ - $Mg_2SiO_4$ , which may be related to the longer average Si-O distances in the spinel phase. Two further weak bands are observed near 455 and 550  $cm^{-1}$ , but there is no indication of the remaining band expected in the Raman

spectrum. The feature near 180  $cm^{-1}$  is not part of the spectrum, but is due to a stray reflection within the spectrometer. The sharp spikes below 100  $cm^{-1}$  are due to plasma lines of the laser and rotational bands of  $N_2$  and  $O_2$  in the air, while the steeply rising background is caused by fluorescence probably due to some trace impurity in the sample.

Jeanloz (1980) obtained the infrared spectrum of  $\beta$ - $Co_2SiO_4$ . He noted a band at 686  $cm^{-1}$ , which he assigned to a symmetric stretching vibration of the  $Si_2O_7$  units present in the  $\beta$ -phase. We observe two bands at 700 and 675  $cm^{-1}$  in the infrared spectrum of  $\beta$ - $Mg_2SiO_4$  (Fig. 4) which might be given the same assignment. However, no analogous bands are observed in the Raman spectrum for  $\beta$ - $Mg_2SiO_4$  (Fig. 4). The  $Si_2O_7$  units in  $\beta$ - $Mg_2SiO_4$  have site symmetry  $C_{2v}$  within a crystal symmetry  $D_{2h}^{28}$  (Horiuchi and Sawamoto, 1981), with two  $Si_2O_7$  units per spectroscopic unit cell. The symmetric stretching vibra-



tion about the bridging oxygen should give rise to two crystal bands with symmetries  $B_{2u}$  and  $A_g$ , one active in the infrared and the other strong in the Raman spectrum. We observe two bands in this region in the infrared spectrum and none in the Raman. From this, it is possible that a description in terms of discrete  $Si_2O_7$  units may not be the best interpretation of the vibrational spectra of  $\beta$ - $Mg_2SiO_4$ . It is of interest that both the infrared and Raman spectra of  $\beta$ - $Mg_2SiO_4$  are similar to those of  $\alpha$ - $Mg_2SiO_4$ . This is reasonable, since a similar number of bands with a similar distribution of symmetry species is predicted in the spectra of both (36 Raman and 38 infrared for  $\alpha$ - $Mg_2SiO_4$ ; 39 Raman and 38 infrared for  $\beta$ - $Mg_2SiO_4$ ). Also the average bond lengths in both are similar (although Si-O is slightly longer and Mg-O shorter in  $\beta$ - $Mg_2SiO_4$ ) even though the structures are significantly different (Horiuchi and Sawamoto, 1981). The major high-frequency bands for  $\beta$ - $Mg_2SiO_4$  do occur at slightly lower frequency than for the  $\alpha$  phase, which may be related to the slight expansion of the  $SiO_4$  units in  $\beta$  relative to  $\alpha$ - $Mg_2SiO_4$ .

For the purposes of the present calculation of vibrational entropies, the observed infrared and Raman spectra have been simplified as described below. We note that a number of inactive modes is predicted for all three  $Mg_2SiO_4$  polymorphs, while not all of the expected active modes have been observed, and that we have no information on the dispersion relations for these modes. These uncertainties limit the rigor with which the vibrational calculations can be performed but, as will be discussed below, useful results can still be obtained.

### *Kieffer's model*

Entropies and heat capacities of the  $Mg_2SiO_4$  polymorphs can be calculated with Kieffer's lattice vibrational model which provides an approximation of the real vibrational spectrum of a mineral (Kieffer, 1979a,b,c, 1980). The thermodynamic functions of a crystal can be expressed as averages over the vibrational density of states. These functions are relatively insensitive to the details of the spectrum, except at low temperature, so Kieffer's approximation generally yields good estimates of the heat capacities and entropies of minerals.

The Kieffer vibrational model takes the vibrational unit of a crystal as the primitive unit cell and has  $3s$  total degrees of freedom associated with it ( $s$  = number of atoms in unit cell). Of the  $3s$  degrees of freedom, only three are acoustic modes, namely two shear modes (S) and one longitudinal (P) mode characterized by acoustic velocities. A simple sine wave dispersion of these modes toward the edge of the Brillouin zone is assumed. The remaining  $3s-3$  modes are optic modes and span a broad range of frequencies. An estimate of the range is obtained from far-infrared, near-infrared and Raman spectra. Little information is available about dispersion of the optic modes across the Brillouin zone for most mineral phases.

Since this is most critical for the lowest frequency mode which greatly affects  $C_P$  at low temperature, the lowest optic mode is assumed to vary inversely with a characteristic mass ratio across the Brillouin zone. The optic modes are distributed uniformly between a lower cutoff frequency,  $\omega_l$ , and an upper cutoff frequency,  $\omega_u$ , specified from spectral data. Any isolated modes (such as Si-O and O-H stretching modes) are represented as separate Einstein oscillators, designated by  $\omega_{E1}$ ,  $\omega_{E2}$ , . . . , or by a second optic continuum. Thus the assumed frequency distribution is a sum of the acoustic branches, optic continuum(a) and Einstein oscillators. Data required for the model are acoustic velocities, crystallographic data and spectroscopic data.

### *General approach to vibration models*

From the discussion above, it is clear that no unique model, incorporating an unequivocal assignment of vibrational modes and specific dispersion relations, can be selected for a complex silicate such as an  $Mg_2SiO_4$  polymorph. Rather a set of related models with small differences in band assignments, partitioning of modes into optic continua and Einstein oscillators, and dispersion relations, can be developed for each phase such that these models are consistent with the observed spectra, acoustic velocities and constraints of crystallographic symmetry. In the sections which follow, we show that such a set of models for the  $Mg_2SiO_4$  polymorphs yield heat capacities and entropies which cluster around (to 5% or better) measured heat capacities and entropies derived above from calorimetry and phase equilibria. Such models, shown in Table 5, are all approximately equally "good" in the sense that they are consistent with both the spectra and the thermochemical data, and we have no way of selecting any as significantly "better". The encouraging feature of these calculations is that, although no single model can be selected, the range of models consistent with spectroscopic data and showing reasonable dispersion relations give values of  $C_P$  and  $S^\circ$  which are relatively insensitive to the details of modelling. Using models with features generally inconsistent with the spectra give a much larger range of  $C_P$  and  $S^\circ$  values and such models will not be considered further except to note that simple Debye models consistently underestimate  $C_P$  and  $S^\circ$  by 10–20% (Watanabe, 1982).

The unknown vibrational parameters, including inactive modes and dispersion relations, clearly constitute a weak point of the modelling. Were these known, the vibrational modelling could proceed entirely independently of the known thermochemical data. However, without such knowledge, we have had to use the observed  $C_P$  and  $\Delta S^\circ$  values to put some bounds on the low frequency cutoff of the optic continuum, especially for  $\gamma$ - $Mg_2SiO_4$  which has the smallest number of bands active in the infrared and Raman.

The model treats each vibration as harmonic and gives

Table 5. Vibrational models for  $Mg_2SiO_4$  polymorphs

Mineral	(0) <sup>a</sup> cm <sup>-1</sup>	$\omega_{k1}$ (k <sub>max</sub> ) <sup>b</sup> cm <sup>-1</sup>	$\omega_{U1}$ <sup>c</sup> cm <sup>-1</sup>	$m_2/m_1$ <sup>d</sup>	$\omega_{22}$ <sup>e</sup> cm <sup>-1</sup>	$\omega_{U2}$ <sup>f</sup> cm <sup>-1</sup>	$q_0$ <sup>g</sup>	$\omega_{E1}$ <sup>h</sup> cm <sup>-1</sup>	$q_1$ <sup>i</sup>	$\omega_{E2}$ <sup>h</sup> cm <sup>-1</sup>	$q_2$ <sup>i</sup>	$\omega_{E3}$ <sup>h</sup> cm <sup>-1</sup>	$q_3$ <sup>i</sup>	$S^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> )			$C_p^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> )		
														298 K	700 K	1000 K	298 K	700 K	1000 K
<b><math>\alpha</math>-<math>Mg_2SiO_4</math></b>																			
Model 1	144	128	620	92/24				950	0.190					23.52	53.12	67.74	27.72	39.05	41.63
Model 2	144	128	620	92/24				837	0.048	930	0.142			23.75	53.48	68.60	28.14	39.27	42.35
Model 3	144	144	620	0/1.0				837	0.048	930	0.142			22.75	52.42	67.04	27.72	39.12	41.70
Model 4	144	128	620	92/24				900	0.095	1000	0.095			23.52	53.12	67.74	27.72	39.05	41.63
Model 5	144	128	620	92/24	850	950	0.19							23.52	52.70	66.90	27.58	38.83	40.44
<b><math>\beta</math>-<math>Mg_2SiO_4</math></b>																			
Model 1	190	167	590	84/24				700	0.025	950	0.210			21.14	50.18	64.68	26.85	38.70	41.37
Model 2	190	178	590	168/24				700	0.030	950	0.200			20.79	49.90	64.40	26.88	38.73	41.40
Model 3	190	178	600	168/24				700	0.050	810	0.095	950	0.095	20.58	49.90	64.47	27.02	38.94	41.51
Model 4	190	167	590	84/24	700	950	0.245							21.07	49.83	64.02	26.88	37.86	40.25
Model 5	190	167	590	84/24	920	950	0.210	700	0.035					20.86	49.34	63.42	26.46	37.58	40.11
<b><math>\gamma</math>-<math>Mg_2SiO_4</math></b>																			
Model 1	240	214	550	92/24				850	0.300					19.74	48.52	62.91	26.32	38.51	41.14
Model 2	240	194	520	46/24				850	0.340					20.30	48.87	63.26	26.11	38.44	41.07
Model 3	220	178	520	46/24				850	0.360					20.44	48.87	63.19	25.90	38.30	41.00
Model 4	260	232	550	92/24	830	850	0.200							20.79	49.22	62.84	27.16	36.90	38.90
Model 5	250	250	520	0/1.0	825	835	0.230							20.30	48.52	62.14	26.81	37.36	38.83

<sup>a</sup> Lower limit of first optic continuum (O.C.) at  $k = 0$ ; <sup>b</sup> Lower limit of first O.C. at  $k_{max}$ ; <sup>c</sup> Upper limit of first O.C.; <sup>d</sup> Mass ratio; <sup>e</sup> Lower limit of second O.C.; <sup>f</sup> Upper limit of second O.C.; <sup>g</sup> Modes partitioned in second O.C.; <sup>h</sup> Einstein oscillators (E.O.'s) 1, 2 and 3; <sup>i</sup> Modes partitioned at E.O.'s 1, 2 and 3. 1 cal = 4.184 joule.

$C_V$ . We have included anharmonicity in the term converting  $C_V$  to  $C_P$  ( $C_P - C_V = TV\alpha/\beta^2$ ). Though this does not entirely take care of possible anharmonic effects at  $T > 1000$  K (especially since  $V(P, T)$  is poorly known), the generally good agreement with experimental thermochemical data suggests that such effects are probably relatively unimportant.

#### Details of vibrational models for the $Mg_2SiO_4$ polymorphs

**Forsterite,  $\alpha$ - $Mg_2SiO_4$ .** Forsterite is orthorhombic and belongs to space group  $Pbnm$  (Brown, 1980). The primitive unit cell contains four formula units. Thus the cell has 28 atoms and 84 degrees of freedom. The unit cell volume is  $290.8 \times 10^{-24}$  cm<sup>3</sup> and the radius of the Brillouin zone (approximated by a sphere) is  $5.89 \times 10^7$  cm<sup>-1</sup>.

Acoustic velocities for forsterite have been thoroughly studied and the following values were used in the model:  $\nu_p = 8.56$  km s<sup>-1</sup>,  $\nu_s = 4.93$  km s<sup>-1</sup> and  $\nu_{max} = 5.00$  km s<sup>-1</sup> (Kieffer, 1980). The corresponding directionally averaged wave velocities are  $\nu_1 = 4.90$  km s<sup>-1</sup>,  $\nu_2 = 4.96$  km s<sup>-1</sup> and  $\nu_3 = 8.56$  km s<sup>-1</sup> (Kieffer, 1979a). These velocities give acoustic branches that reach 89, 99 and 171 cm<sup>-1</sup> at the Brillouin zone boundary.

Features of the forsterite spectra (Fig. 4) that should be noted for the lattice vibrational models are the two distinct bands of frequencies ranging from 144 to 620 cm<sup>-1</sup> and 830 to 985 cm<sup>-1</sup>. Models for  $\alpha$ - $Mg_2SiO_4$  which fit experimental  $C_p^\circ$  and  $S^\circ$  data (Orr, 1953; Robie et al., 1978; Watanabe, 1982) within 2–3% are presented in Table 5. All models have an optic continuum ranging from 144 cm<sup>-1</sup> (lowest optical mode at  $k = 0$ ) to 620 cm<sup>-1</sup>. The high frequency bands which are due to [SiO<sub>4</sub>] stretching vibrations can be represented by one Einstein oscillator, two oscillators or a second optic continuum. Using the partitioning method of Kieffer (1979b), 19% of the total degrees of freedom are assigned to these high frequency modes.

In the majority of models studied, the lower limit of the optic continuum at  $k = 0$ , 144 cm<sup>-1</sup>, was dispersed to 128 cm<sup>-1</sup> at the

Brillouin zone boundary. The characteristic mass ratio of 92/24 corresponds to the assumption that the low frequency vibration can be described as a Mg atom vibrating against a [SiO<sub>4</sub>] tetrahedron. A lattice dynamical calculation of forsterite by Iishi (1978) supports this assumption.

Models with the optic continuum extending from 620 cm<sup>-1</sup> to 128 cm<sup>-1</sup> at  $k_{max}$  show very good agreement with experimental heat capacity data. These models, however, tend to overestimate entropies slightly, implying that the lower limit of 128 cm<sup>-1</sup> for the optic continuum is too low. An excellent fit to the entropy data can be obtained if the lowest optical mode at  $k = 0$ , 144 cm<sup>-1</sup>, is not dispersed at all across the Brillouin zone (Table 5:  $\alpha$ - $Mg_2SiO_4$ , Model 3). However, the 144 cm<sup>-1</sup> mode is not certain and has only been seen by Oehler and Günthard (1969). Our Far-infrared spectrum of  $\alpha$ - $Mg_2SiO_4$  is not definitive in this region.

The distribution of modes in the far-infrared spectral region (at  $k_{max}$ ) is critical in the calculation of entropies.  $S^\circ$  and  $C_p^\circ$  increase as the lower limit of the optic continuum at  $k = 0$  is dispersed to lower values at  $k_{max}$ . Models for  $\alpha$ - $Mg_2SiO_4$  in Table 5 demonstrate that  $C_p^\circ$  and  $S^\circ$  are much less sensitive to details of the high frequency part of the spectrum. Variation in the placement of Einstein oscillators and distribution of modes between oscillators have negligible effect upon  $C_p^\circ$  and  $S^\circ$ . In addition, little difference in  $C_p^\circ$  and  $S^\circ$  is found whether one Einstein oscillator or two oscillators are used to model the high frequency [SiO<sub>4</sub>] stretching modes. Finally,  $\alpha$ - $Mg_2SiO_4$  can be modelled with two optic continua (Table 5:  $\alpha$ - $Mg_2SiO_4$ , Model 5). Model 5 shows generally good agreement with the heat capacity and entropy data.

**Modified spinel,  $\beta$ - $Mg_2SiO_4$ .** Modified spinel,  $\beta$ - $Mg_2SiO_4$ , is orthorhombic and belongs to space group  $Imma$  (Horiuchi and Sawamoto, 1981). The primitive unit cell, which is half the size of the conventional body-centered cell, has four formula units, 28 atoms and hence 84 degrees of freedom. The unit cell volume is  $269.1 \times 10^{-24}$  cm<sup>3</sup> and the Brillouin zone radius is  $6.04 \times 10^7$  cm<sup>-1</sup>.

Unlike those of forsterite, the acoustic velocities of  $\beta$ - $Mg_2SiO_4$  have not been thoroughly studied. Using data from germanate compounds analogous to the  $Mg_2SiO_4$  polymorphs (Liebermann,

1973, 1975), the compressional and shear wave velocities of  $\beta$ - $Mg_2SiO_4$  were estimated to be  $v_p = 9.6 \text{ km s}^{-1}$  and  $v_s = 5.4 \text{ km s}^{-1}$ . These velocities give acoustic branches that reach 198 and  $116 \text{ cm}^{-1}$  at the Brillouin zone boundary. Features of the  $\beta$ - $Mg_2SiO_4$  spectra (Fig. 4) that should be noted for modelling are the lowest frequency band at  $190 \text{ cm}^{-1}$ , the continuous range of modes to  $590\text{--}600 \text{ cm}^{-1}$ , the band at  $700 \text{ cm}^{-1}$  and the higher frequency modes between  $800$  and  $1100 \text{ cm}^{-1}$ .

Experimental heat capacity and entropy data for  $\beta$ - $Mg_2SiO_4$  are much more limited than those for forsterite. In this investigation, two sources were used to provide data for comparison with model calculations: Watanabe's (1982) heat capacity data from  $350\text{--}700 \text{ K}$  obtained from differential scanning calorimetry and an estimate of  $S_{1000}^\circ$  based on a combination of solution calorimetric experiments and phase equilibria studies of the  $Mg_2SiO_4$  polymorphs (see above). One should note that Watanabe's (1982) heat capacity data for forsterite are systematically 1% higher than Orr's (1953) heat capacity data. This raises the possibility that Watanabe's heat capacities for  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  may likewise be systematically high. Thus a 3–4% difference between  $C_p^\circ$  calculated from the models and measured by Watanabe may in fact represent good agreement between calculation and experiment, when errors in both are considered.

Models for  $\beta$ - $Mg_2SiO_4$  which show good agreement with the experimental data are presented in Table 5. These models all have a common feature—an optic continuum ranging from  $590\text{--}600$  to  $190 \text{ cm}^{-1}$  (at  $k = 0$ ).

A number of different mass ratios were tried in dispersing the lowest optical mode at  $k = 0$ ,  $190 \text{ cm}^{-1}$ , across the Brillouin zone to  $k_{\text{max}}$ . Mass ratios of 168/24 and 84/24 provided the best fit with experimental data. These mass ratios were obtained by assuming that a Mg atom vibrating against the  $[Si_2O_7]$  cluster or part of the cluster is involved in the low frequency mode. With dispersion taken into account, the optic continuum is extended from  $590 \text{ cm}^{-1}$  to  $178 \text{ cm}^{-1}$  (for  $m_2/m_1 = 168/24$ ) or  $167 \text{ cm}^{-1}$  (for  $m_2/m_1 = 84/24$ ) at  $k_{\text{max}}$ . Models which disperse the low frequency mode lower than  $167 \text{ cm}^{-1}$  yield values inconsistent with observed  $C_p^\circ$  and  $S^\circ$  values. This offers support for not including the questionable  $130 \text{ cm}^{-1}$  band (Fig. 4 and Table 4) in the vibrational models for  $\beta$ - $Mg_2SiO_4$ .

Enumeration of the silicon-oxygen stretching modes in  $\beta$ - $Mg_2SiO_4$  is more complex than in  $\alpha$ - $Mg_2SiO_4$  because there are Si–O bridging (Si–O<sub>br</sub>) as well as Si–O nonbridging (Si–O<sub>nbr</sub>) bonds. Following the methodology presented by Kieffer (1980) for the chain silicates, each  $Si_2O_7$  group has two Si–O<sub>br</sub> and six Si–O<sub>nbr</sub> bonds. Si–O<sub>br</sub> bonds give rise to two symmetric and two antisymmetric vibrations while the six Si–O<sub>nbr</sub> bonds give rise to six vibrations—a total of ten vibrations per  $Si_2O_7$  unit. The fraction of modes partitioned at the higher frequencies (i.e.,  $700\text{--}1100 \text{ cm}^{-1}$ ) is therefore  $5/21 = 24\%$ .

The high frequency (Si–O<sub>nbr</sub>)<sub>3</sub> stretching modes ranging from  $800\text{--}1100 \text{ cm}^{-1}$  can be adequately represented by one or two Einstein oscillators or a second optic continuum (Table 5:  $\beta$ - $Mg_2SiO_4$ , Models 2, 3 and 5). The (Si–O<sub>br</sub>) stretching frequency at  $700 \text{ cm}^{-1}$ , can be represented by an Einstein oscillator at  $700 \text{ cm}^{-1}$ . An alternative method of representing the (Si–O<sub>br</sub>) and (Si–O<sub>nbr</sub>) stretching modes is to place them in a second optic continuum extending from  $700$  to  $950 \text{ cm}^{-1}$  (Table 5:  $\beta$ - $Mg_2SiO_4$ , Model 4).

*Spinel,  $\gamma$ - $Mg_2SiO_4$ .*  $\gamma$ - $Mg_2SiO_4$  is cubic and crystallizes with the well-known spinel structure that belongs to space group  $Fd3m$  (Sasaki et al., 1982). The primitive unit cell is one quarter

of the size of the face-centered cell and has two formula units, 14 atoms and thus 42 degrees of freedom. The volume of the primitive unit cell is  $132.0 \times 10^{-24} \text{ cm}^3$  and the Brillouin zone radius is  $7.65 \times 10^7 \text{ cm}^{-1}$ .

As in the case of  $\beta$ - $Mg_2SiO_4$ , data from germanate analogue compounds must be used to estimate the compressional and shear wave velocities of  $\gamma$ - $Mg_2SiO_4$  (Liebermann, 1973, 1975). Values of  $v_p$  and  $v_s$  are estimated to be  $9.8$  and  $5.4 \text{ km s}^{-1}$ , respectively. These velocities give acoustic branches that reach  $255$  and  $140 \text{ cm}^{-1}$  at the Brillouin zone boundary.

Features of the  $\gamma$ - $Mg_2SiO_4$  spectra (Fig. 4) noted for the lattice vibrational models are the strong absorption peaks between  $800$  and  $840 \text{ cm}^{-1}$  and the weaker bands ranging from  $350$  to  $550 \text{ cm}^{-1}$ . Because  $\gamma$ - $Mg_2SiO_4$  has high symmetry, many vibrational modes are inactive in both infrared and Raman. This lends a high uncertainty to defining the position of the lowest optic mode and thus the models for  $\gamma$ - $Mg_2SiO_4$  are less constrained than for  $\alpha$ - or  $\beta$ - $Mg_2SiO_4$ .

Watanabe's (1982) heat capacity data and an estimate of  $S_{1000}^\circ$  based on calorimetry and phase equilibria studies were used to discriminate between "reasonable" and "outlandish" vibrational models of  $\gamma$ - $Mg_2SiO_4$ . A variety of models were found to show good agreement with the experimental data (Table 5). All the models have an optic continuum spanning the lower frequency range while the high frequency Si–O stretching vibrations are represented by either an Einstein oscillator or a second continuum.

### Constraints on lattice entropies

As pointed out above, there are a number of models for each polymorph which show good agreement with the available heat capacity and entropy data. Figure 5 shows

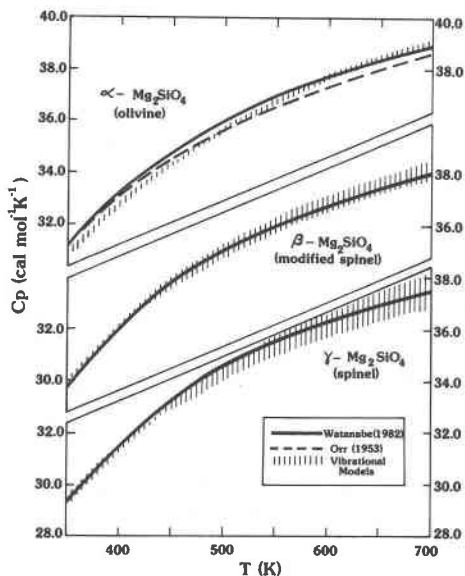


Fig. 5. Heat capacities of the  $Mg_2SiO_4$  polymorphs as functions of temperature. Dashed curve represents Orr's (1953) forsterite data while solid curves represent experimental data from Watanabe (1982). Hatched lines represent the heat capacities estimated from vibrational models, as discussed in text.

Table 6. Standard entropies of  $Mg_2SiO_4$  polymorphs

	$S_{298}^0$ <sup>a</sup>	$S_{1000}^0$ <sup>a</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )	$S_{1000}^0$
Olivine ( $\alpha$ )			
Model 3	22.75	52.42	67.04
Experimental	22.75	51.82	66.24
Modified Spinel ( $\beta$ )			
Models (Average)	20.89	49.80	64.20
Spinel ( $\gamma$ )			
Models (Average)	20.31	48.79	62.87

<sup>a</sup> 1 cal = 4.184 joule.

the range in  $C_p$ 's predicted from the models and their agreement with the experimental  $C_p$  data. Models predict  $C_p$  values within 2–3% of the experimental data for each polymorph.

Entropies of the  $Mg_2SiO_4$  polymorphs based on the vibrational models are shown in Table 6. The entropies tabulated for  $\alpha$ - $Mg_2SiO_4$  are based on Model 3 (see above) which shows the best agreement with the entropy of forsterite from 300 to 1000 K. Since high temperature entropy data are available for  $\alpha$ - $Mg_2SiO_4$ , better constraints can be imposed on forsterite than the other two polymorphs. The entropies for  $\beta$ - and  $\gamma$ - $Mg_2SiO_4$  in Table 5 are based on averages of the models in Table 5 since all these models are consistent with the spectra and thermodynamic data. It is encouraging to note that these entropies from the various models are within 2% for  $\beta$ - $Mg_2SiO_4$  and 3% for  $\gamma$ - $Mg_2SiO_4$ .

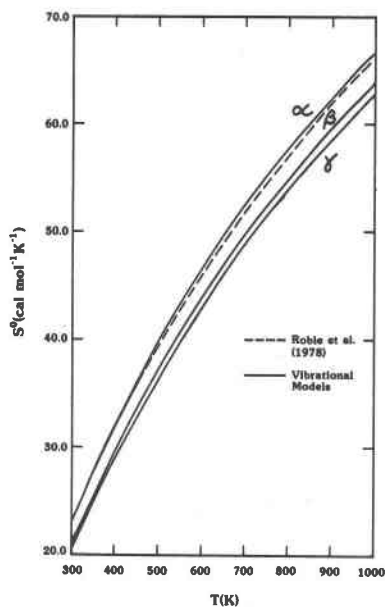


Fig. 6. Standard entropies ( $S_T^0$ ) of  $Mg_2SiO_4$  polymorphs, calculated from vibrational models (solid curves), as functions of temperature. Experimental standard entropy of  $\alpha$ - $Mg_2SiO_4$  (Orr, 1953; Robie et al., 1978) is shown as dashed curve.

Entropies for the  $Mg_2SiO_4$  polymorphs are plotted as a function of temperature in Figure 6. This shows one of the advantages of the vibrational calculations—estimates of  $S^0$  and  $C_p^0$  can be obtained for temperatures where experimental data are not available. At high temperatures ( $>700$  K), anharmonicity begins to play a significant role. Thermal expansion data and bulk modulus values used in the correction of  $C_v$  to  $C_p$  are listed in Table 3. At 1000 K, this correction increases the entropy by roughly 0.3 to 0.5%.

The entropies of transition at 1000 K based on the vibrational calculations for  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  are  $-2.8 \pm 0.6$  and  $-1.3 \pm 0.9$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. These compare well with the  $\Delta S^0$  values based on the combination of calorimetry and phase equilibria data which give  $-2.5 \pm 0.5$  cal mol<sup>-1</sup> K<sup>-1</sup> for the  $\alpha \rightarrow \beta$  transition and  $-1.5 \pm 0.9$  cal mol<sup>-1</sup> K<sup>-1</sup> for the  $\beta \rightarrow \gamma$  transition.

### Conclusions—utility of vibrational modelling

This study has shown that a range of reasonable vibrational models can be obtained for the  $Mg_2SiO_4$  polymorphs from the appropriate crystallographic, acoustic shear wave, and spectral data. Heat capacities and entropies estimated by the models are found to be in good agreement with available experimental data. In addition, models which predict heat capacities within 2–3% of the measured values at 298–700 K also predict entropies which fall within a range of about 3%. That is, although the vibrational models may differ in details such as the choice of dispersion constants, optic continua versus Einstein oscillators, and partitioning of the modes, the calculated entropies are not overly sensitive to these details.

The consistency of the vibrational and thermochemical estimates of entropies encourages us to attempt similar vibrational calculations for other phases occurring at even higher pressures; e.g., silicate ilmenites, perovskites and garnets. The amount of material needed for infrared and Raman spectroscopy is much smaller than that needed for solution calorimetry. Thus vibrational calculations may provide constraints on the entropies of such transitions when no other data can be obtained. Using such an approach, with very crude estimates of the spectra of  $MgSiO_3$  ilmenite and perovskite, we predict a negative  $P$ - $T$  slope for the ilmenite  $\rightarrow$  perovskite transition. However, this preliminary calculation needs further refinement and better spectral data.

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