

# Study of the MgGeO<sub>3</sub> polymorphs (orthopyroxene, clinopyroxene, and ilmenite structures) by calorimetry, spectroscopy, and phase equilibria

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## ABSTRACT

Below 6 GPa, MgGeO<sub>3</sub> transforms with increasing pressure from an orthopyroxene, to a clinopyroxene, and finally to an ilmenite structure. Thermodynamic parameters for MgGeO<sub>3</sub> (opx → cpx) and MgGeO<sub>3</sub> (cpx → ilm) have been constrained by high-temperature solution calorimetric experiments, lattice vibrational calculations, and phase-equilibrium studies. The enthalpy and entropy of MgGeO<sub>3</sub> (opx → cpx) determined in this study are  $-3440 \pm 681 \text{ J} \cdot \text{mol}^{-1}$  and  $-1.5$  to  $-3.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , respectively, which are comparable in magnitude to values for other phase transitions among pyroxenes and pyroxenoids. The values of  $\Delta H_{973}^0$  and  $\Delta S_{973}^0$  for MgGeO<sub>3</sub> (cpx → ilm) determined from calorimetry and lattice vibrational calculations are  $7808 \pm 561 \text{ J} \cdot \text{mol}^{-1}$  and  $-7.5 \pm 1.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , respectively. These values are consistent with new experimental reversals of the MgGeO<sub>3</sub> (cpx → ilm) phase boundary,  $P$  (in GPa) =  $1.913 + 0.0018T$  (in K).

## INTRODUCTION

In recent years, great progress has been made in the study of high-pressure phase transitions among silicates (e.g. Ito and Takahashi, 1987). However, although phase relations among high-pressure silicate phases have been roughly mapped out, detailed reversals of phase-equilibrium boundaries remain largely unattained, and some compounds cannot be quenched to ambient conditions. Germanates are often used as geochemical models for silicates since they show similar transitions as silicates but at much lower pressures.

The MgGeO<sub>3</sub> polymorphs have been used as analogues for the MgSiO<sub>3</sub> polymorphs and transform with increasing pressure from the structure of orthopyroxene to clinopyroxene to ilmenite. Two studies have reported the phase relations among the MgGeO<sub>3</sub> at high pressures and temperatures. The results presented by Kirfel and Neuhaus (1974) are shown in Figure 1A. They found that the orthopyroxene stability field is limited to low pressures and temperatures, whereas clinopyroxene is stable at high temperatures and pressures. At higher pressures, clinopyroxene transforms to ilmenite. Ozima and Akimoto's (1983) topology for the orthopyroxene-clinopyroxene boundary differs greatly from that of Kirfel and Neuhaus (Fig. 1B). They found that orthopyroxene is stable at high temperatures and low pressures and has a greater stability field than that reported by Kirfel and Neuhaus (1974).

The purpose of this study is to resolve these discrepancies and to derive a self-consistent set of thermody-

amic parameters for the orthopyroxene to clinopyroxene boundary as well as the clinopyroxene-ilmenite phase boundary. The method used is similar to that reported by Ross and Navrotsky (1987). The previous experiments are analyzed for internal consistency, and the set of enthalpies and entropies of transition consistent with each data set is determined. These results are compared with independent determinations of the enthalpies of transition from high-temperature solution calorimetry as well as independent calculations of entropies of transition from lattice vibrational models. In addition, the results from a new phase-equilibrium study of the clinopyroxene-ilmenite boundary are reported. Finally, the use of MgGeO<sub>3</sub> polymorphs as analogues for MgSiO<sub>3</sub> polymorphs is discussed.

## EXPERIMENTAL METHODS

### Sample synthesis

Orthopyroxene (about 2 g) was synthesized from a mixture of reagent-grade MgO and GeO<sub>2</sub> heated at 1273 K for 20 h. The product was examined by powder X-ray diffraction and confirmed to be orthopyroxene; all of the lines in the pattern correspond closely in  $d$  spacings and intensities to an "orthoenstatite-type" MgGeO<sub>3</sub> belonging to space group *Pbca* with  $a = 18.80 \text{ \AA}$ ,  $b = 8.95 \text{ \AA}$ , and  $c = 5.34 \text{ \AA}$  (Ozima and Akimoto, 1983). Clinopyroxene (about 250 mg) was synthesized from the orthopyroxene in a girdle anvil press operated at 2 GPa and 1273 K for 8 h. Microscopic examination of the run products showed that they included traces of Pt from the Pt capsules. The Pt was carefully removed by hand so that none was visible optically or could be detected by X-ray diffraction. Powder X-ray diffraction confirmed that the run products were pure clinopyroxene, and all peaks in the pattern showed excellent agreement with the  $d$

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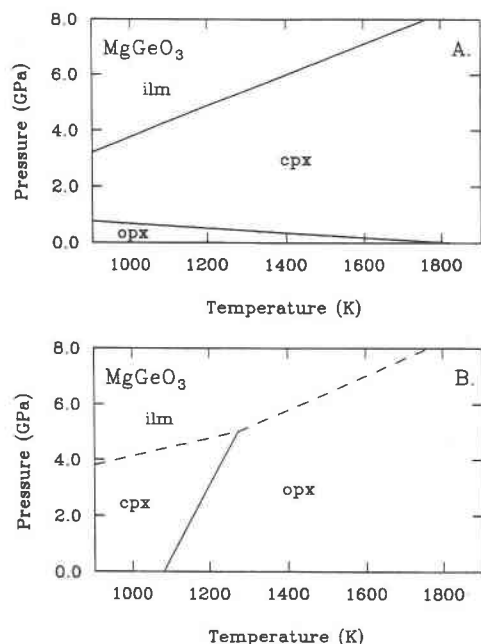


Fig. 1. Previous phase relations proposed for the MgGeO<sub>3</sub> polymorphs: (A) Kirfel and Neuhaus (1974) and (B) Ozima and Akimoto (1983).

spacings and intensities reported by Ozima and Akimoto (1983) for a *C2/c* clinopyroxene with  $a = 9.60 \text{ \AA}$ ,  $b = 8.93 \text{ \AA}$ ,  $c = 5.16 \text{ \AA}$ , and  $\beta = 101^\circ$ . Ilmenite (about 260 mg) was synthesized from orthopyroxene at 6 GPa and 1273 K for 8 h using the girdle anvil press. As in the clinopyroxene runs, traces of Pt were removed by hand from the recovered samples. Powder X-ray diffraction and optical examination confirmed that the run products were pure ilmenite, with no reactant remaining.

### Calorimetry

Calorimetric runs were made using a twin Calvet-type microcalorimeter (Navrotsky, 1977). Enthalpies of solution for the three polymorphs were measured in molten lead borate, 2PbO·B<sub>2</sub>O<sub>3</sub>, at 973 K. At that temperature each MgGeO<sub>3</sub> phase persists unchanged in the calorimeter prior to dissolution. The clinopyroxene and ilmenite samples dissolved rather sluggishly and incompletely, even when using sample containers with perforated Pt-foil bottoms (Navrotsky et al., 1980). Therefore a layer of alumina (about 20–25 mg) was placed in the bottom of the sample container, and the 15 to 25 mg of MgGeO<sub>3</sub> sample was sprinkled on top of the alumina base. The readily dissolving alumina helped to introduce the sample into the flux, greatly reducing the dissolution time and promoting complete dissolution of the germanate. The heat of solution for pure alumina was measured, and the heats of solution for MgGeO<sub>3</sub> clinopyroxene and ilmenite were calculated by subtracting  $\Delta H_{\text{alumina}}$  from  $\Delta H_{\text{total}}$ . Heats of solution of MgGeO<sub>3</sub> orthopyroxene, clinopyroxene, and ilmenite are shown in Table 1.

### Spectroscopy

All vibrational spectra presented for the MgGeO<sub>3</sub> polymorphs were obtained on polycrystalline samples. Infrared spectra were obtained using a Nicolet 7199 optical bench and a Nicolet 1280 data processor. Far-infrared spectra between 100 and 400 cm<sup>-1</sup> were obtained with a liquid He-cooled Ge-bolometer (Infrared

TABLE 1. Enthalpies of solution of the MgGeO<sub>3</sub> polymorphs, orthopyroxene, clinopyroxene and ilmenite, in 2PbO·B<sub>2</sub>O<sub>3</sub> at 973 K

Orthopyroxene		Clinopyroxene		Ilmenite	
Mass (mg)	$\Delta H_{\text{soln}}^{\circ}$ (J·mol <sup>-1</sup> )	Mass (mg)	$\Delta H_{\text{soln}}^{\circ}$ (J·mol <sup>-1</sup> )	Mass (mg)	$\Delta H_{\text{soln}}^{\circ}$ (J·mol <sup>-1</sup> )
22.81	31112	18.70	36660	19.33	29547
22.00	32342	15.10	35150	20.52	29535
22.08	32510	15.06	36832	16.47	29259
22.52	32541	16.81	35405	14.00	27953
21.85	31966	15.64	37305	16.68	28593
23.15	35054	14.36	37999	16.53	27619
23.38	35903				
25.66	31539				
20.88	35271				
22.95	32455				
20.46	33627				
33120 ± 486*		36560 ± 448*		28752 ± 339*	

\* Average; error represents one standard deviation of the mean.

TABLE 2. Peak positions, in wave numbers (cm<sup>-1</sup>), from infrared and Raman spectra of MgGeO<sub>3</sub> orthopyroxene, clinopyroxene, and ilmenite structures

Orthopyroxene		Clinopyroxene		Ilmenite	
Infra-red	Raman	Infra-red	Raman	Infra-red	Raman
	107				
	118 st		121		
	130				
	138 w				
	145 w				
	157 w				
	165		171		
	181		187		
	190		198		204 st
	206		217		
232	226 w	227	230 w		
247	236	256	265		266 w
256	268		271 w		
283	276 sh	280 sh	280		
295 br	293	290	294		
316	327	314 br	328		315
337	344	341	348		332
343	362 sh		358	368	
377	369	380 br			378
387 br	402	417	405 st	403	
414	408 sh	425 sh			
426	422	434 w			
437	445			449	
455 br	460 br	460	466		453
488 sh	477				475
495	498 w	482 br	488 w		
517 sh					
539	541	555	578 st	550	
552		602		603	
580	573 st				613 w
714	711	707	703	695 st	
737	745 w	746 br	734 w		722 st
787	784				
	798 w	797			
	821 sh				
841 w	830		816		
	864	865 st	859 st		
876 st	880 st				
908 sh	903 sh				

Note: w = weak; st = strong; br = broad; sh = shoulder.

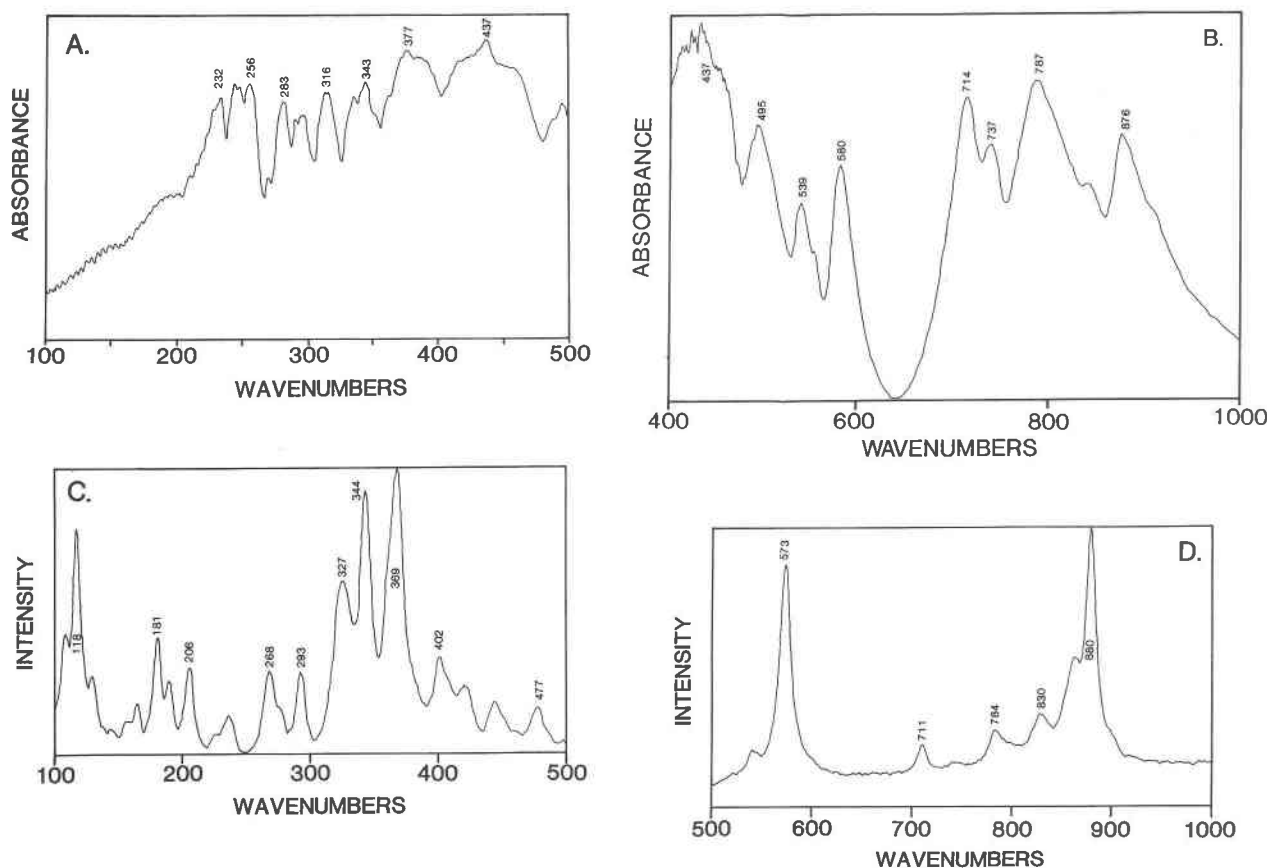


Fig. 2. Vibrational spectra of MgGeO<sub>3</sub> orthopyroxene: (A) far-infrared, (B) mid-infrared, (C) low-frequency Raman, and (D) high-frequency Raman.

Laboratories) from 1.0 to 2.0 mg of powdered samples mounted on polyethylene plates with Vaseline petroleum jelly. Mid-infrared spectra were obtained above 400 cm<sup>-1</sup> using a HgCdTe liquid N<sub>2</sub>-cooled detector from KBr discs with 0.5 to 1.0 mg of sample per 50 mg of KBr. Raman spectra of the MgGeO<sub>3</sub> polymorphs were measured with a micro-Raman spectrometer consisting of a Spex 1877 triple spectrograph, an optical-scanning multichannel analyzer (OSMA; Princeton Instruments) and an Ar<sup>+</sup> laser for sample excitation (Mao et al., 1985). All samples were stable under high laser power. Far-infrared, mid-infrared, and Raman spectra of MgGeO<sub>3</sub> orthopyroxene, clinopyroxene, and ilmenite are shown in Figures 2, 3 and 4, respectively, and peak positions are listed in Table 2.

#### Phase-equilibria experiments

The phase-equilibria experiments at high temperatures and pressures were carried out with SAM-85, a high-pressure apparatus consisting of a 250-ton press with a cubic anvil device of the DIA type, at the Stony Brook High Pressure Laboratory. Anvils with a 6-mm edge length were used in the experiments for studying the pressure and temperature regime from 3 to 6 GPa and 1000 to 1500 K, respectively. The cell assembly consisted of a pyrophyllite cube, prefired at 973 K for 10 min, inside of which a cylindrical graphite furnace fitted with a sleeve and two inserts of NaCl served as a capsule for the sample. The run temperatures were measured in the central part of the sample with a Pt-Pt<sub>87</sub>Rh<sub>13</sub>

thermocouple without any correction for the pressure effect on the electromotive force of the thermocouple. The uncertainty in the temperature readings was ± 5 K. Sample pressure versus run load has been calibrated at room temperature with the Bi I-II (2.55 GPa), Th I-II (3.67 GPa), Ba I-II (5.5 GPa), and Bi III-V (7.7 GPa) transitions and at 1273 K using the quartz-coesite (Bohlen and Boettcher, 1982), Fe<sub>2</sub>SiO<sub>4</sub> olivine-spinel (Yagi et al., 1987), and CaGeO<sub>3</sub> garnet-perovskite (Susaki et al., 1985) transitions (Gwanmesia, 1987). The uncertainty in pressure is estimated to be ± 0.1 GPa.

Starting material for each run was 50-50 mixture of MgGeO<sub>3</sub> clinopyroxene and ilmenite. The samples were held at the desired pressure for a time interval of 45 to 240 min, depending on temperature, and then quenched under pressure. After the run, the quenched sample was examined by powder X-ray diffraction and optical microscopy. Run times were long enough to ensure complete conversion to either clinopyroxene or ilmenite. The individual runs are summarized in Table 3.

## RESULTS

### Orthopyroxene to clinopyroxene transition

The results from the two previous experimental studies of the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene phase transition are presented in Figure 5A. Kirfel and Neuhäus's (1974) experiments were synthesis runs using poly-

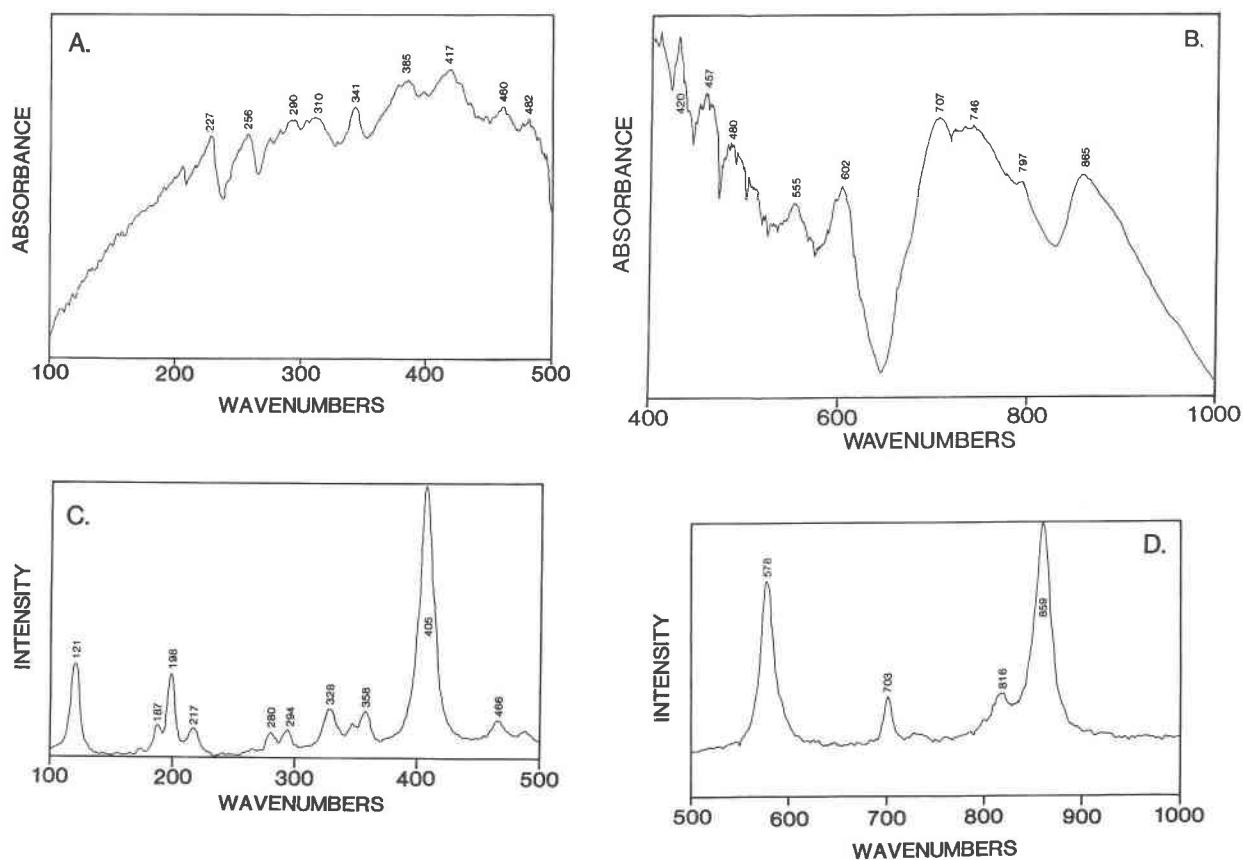


Fig. 3. Vibrational spectra of MgGeO<sub>3</sub> clinopyroxene: (A) far-infrared, (B) mid-infrared, (C) low-frequency Raman, and (D) high-frequency Raman.

crystalline orthopyroxene (in all runs but one) as the starting product. Ozima and Akimoto (1983) attempted high-pressure, high-temperature reversals with single crystals of MgGeO<sub>3</sub> orthopyroxene and clinopyroxene grown from a Li-Mo-V oxide flux as starting materials and quenched their runs to ambient conditions. Kirfel and Neuhaus (1974) observed a narrow stability field for

orthoenstatite-type MgGeO<sub>3</sub> below 1 GPa and a shallow negative slope,  $-0.0008 \text{ GPa} \cdot \text{K}^{-1}$ , for the phase boundary. Ozima and Akimoto (1983), however, observed a larger stability field for orthoenstatite-type MgGeO<sub>3</sub> and a steeper, positive slope,  $0.0263 \text{ GPa} \cdot \text{K}^{-1}$ , for the phase boundary. The  $P$ - $T$  boundaries reported by Kirfel and Neuhaus (1974) and Ozima and Akimoto (1983) are  $P$  (in GPa) =  $1.499 - 0.0008 T$  (in K) and  $P$  (in GPa) =  $-28.50 + 0.0263 T$  (in K), respectively. We have obtained quantitative estimates of  $\Delta H^0$  and  $\Delta S^0$  for the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene transition from a self-consistency analysis (Gordon, 1973) of the  $P$ - $T$  runs reported by these workers. This method is described in detail by Ross and Navrotsky (1987), who were the first to apply self-consistency analysis to the study of high-pressure phase transitions. Parameters used in the analyses are given in Table 4, and results are shown in Figure 6. As expected, no values of  $\Delta H^0$  and  $\Delta S^0$  are consistent with both Kirfel and Neuhaus's (1974) study and Ozima and Akimoto's (1983) study. The data reported in each study, however, were found to be internally consistent. Values of  $\Delta H^0$  and  $\Delta S^0$  consistent with Kirfel and Neuhaus's (1974) study and Ozima and Akimoto's (1983) study. The data reported in each study, however, were

TABLE 3. Results of MgGeO<sub>3</sub> clinopyroxene-ilmenite phase-equilibria experiments

Pressure (GPa)	Temperature (K)	Time (h)	Run product
3.55	1098	8	Clinopyroxene
3.82	1098	22	Clinopyroxene
4.35	1098	24	Ilmenite
4.08	1098	22	Ilmenite
3.82	1382	6	Clinopyroxene
4.88	1382	5.5	Ilmenite
4.35	1382	3	Clinopyroxene
4.61	1382	3	Ilmenite
4.88	1523	1	Ilmenite
4.48	1598	1	Clinopyroxene

Note: Starting compositions were 50-50 mixtures of clinopyroxene and ilmenite. The uncertainties in the pressures and temperatures are  $\pm 0.1$  GPa and  $\pm 5$  K, respectively.

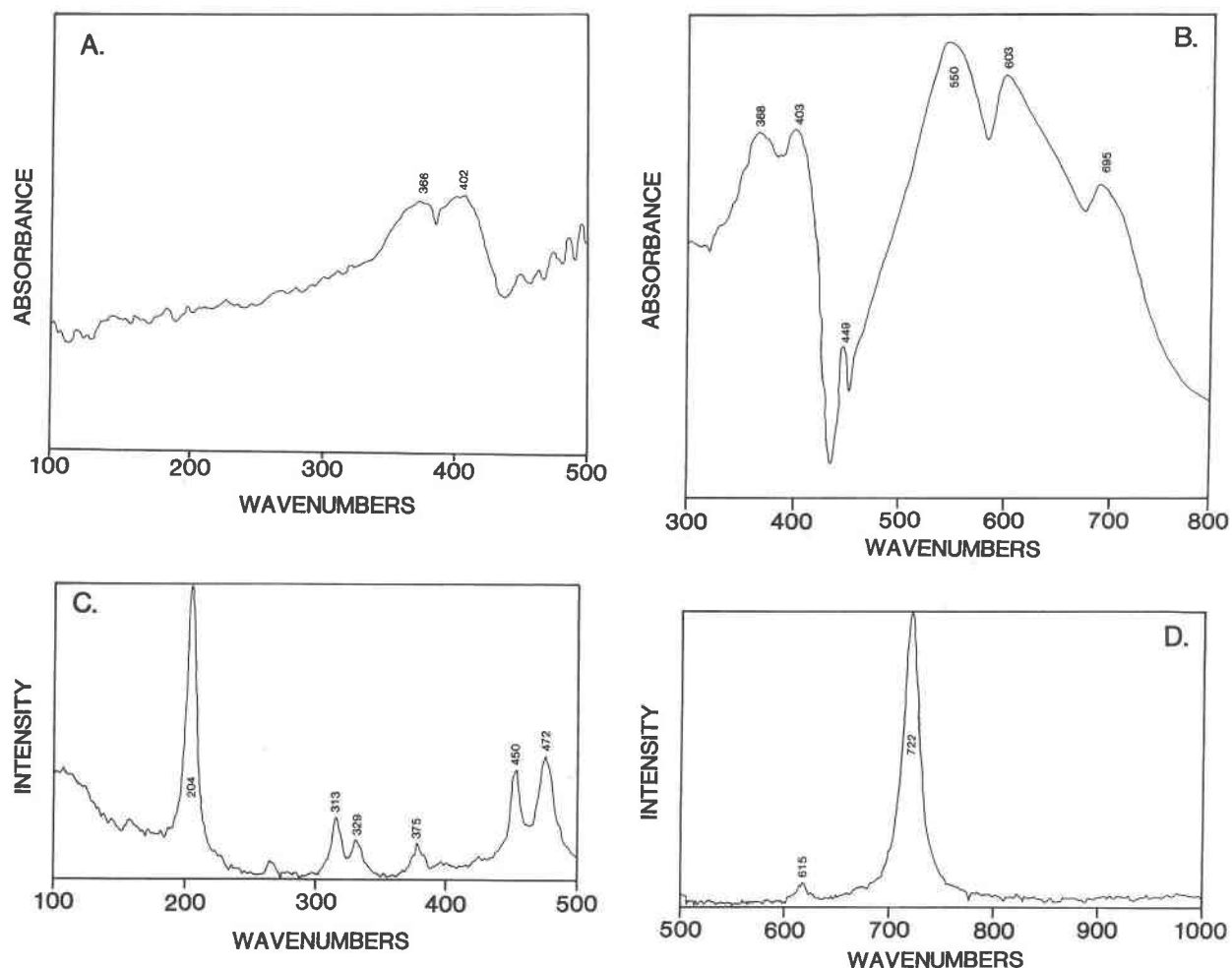


Fig. 4. Vibrational spectra of MgGeO<sub>3</sub> ilmenite: (A) far-infrared, (B) mid-infrared, (C) low-frequency Raman, and (D) high-frequency Raman.

found to be internally consistent. Values of  $\Delta H^0$  and  $\Delta S^0$  consistent with Kirfel and Neuhaus's (1974) data are slightly positive and range from 400 to 1675 J·mol<sup>-1</sup> and 0.4 to 1.3 J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively. Ozima and Akimoto's (1983) data are consistent with negative and much larger values of  $\Delta H^0$  and  $\Delta S^0$ , which can range from -12550 to -52300 J·mol<sup>-1</sup> and -14.6 to -48.9 J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively.

Navrotsky (1981) noted that transitions among pyroxenes and pyroxenoids generally have small values of  $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta V^0$  and that  $\Delta H^0$  and  $T\Delta S^0$  appear to be comparable in magnitude at temperatures of 1000 to 1500 K. In addition, density appears to increase in the order pyroxenoid, orthopyroxene, clinopyroxene; and the thermodynamic data suggest that when the clinopyroxene is the phase with the lowest enthalpy, it is also the phase with lowest entropy. Kirfel and Neuhaus's (1974) data are consistent with these trends in the following ways. The values of  $\Delta H^0$  and  $\Delta S^0$  that are consistent with their data are quite small,  $\Delta H^0$  and  $T\Delta S^0$  are the same mag-

nitude at 1000 K, and clinopyroxene is stable at higher pressures than orthopyroxene (i.e., it has a greater density than orthopyroxene). However, they find that clinopyroxene is stable at higher temperatures than orthopyroxene, suggesting it is the phase of higher entropy. The values of  $\Delta H^0$  and  $\Delta S^0$  found to be consistent with Ozima and Akimoto's (1983) data are much larger than those reported for other pyroxene and pyroxenoid phase transitions (Navrotsky, 1981). However,  $\Delta H^0$  and  $T\Delta S^0$  are approximately equal at 1000 K, clinopyroxene is stable at higher pressures than orthopyroxene, and orthopyroxene is stable at higher temperatures, suggesting that orthopyroxene is the phase of higher entropy.

The results from high-temperature solution calorimetry provide an independent measure of the enthalpy of the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene transition at room pressure and 973 K. At this temperature, Kirfel and Neuhaus (1974) found that orthopyroxene was stable, whereas Ozima and Akimoto (1983) found that clinopyroxene was stable. The results from the calorimetric

experiments (Table 1) indicate clinopyroxene is the phase of lower enthalpy and is stable energetically relative to orthopyroxene at 973 K, which is consistent with Ozima and Akimoto's (1983) study. However, the calorimetric value of  $\Delta H_{973}^0$ ,  $-3440 \pm 661 \text{ J}\cdot\text{mol}^{-1}$ , is only one-third of the smallest value found to be consistent with Ozima and Akimoto's (1983) study (Fig. 6). This value, on the other hand, is similar to that found for other pyroxene and pyroxenoid transitions (Navrotsky, 1981).

Two methods can be used to determine the entropy of the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene phase transition. First,  $\Delta S^0$  can be calculated from lattice vibrational models formulated from the infrared and Raman spectra of the two polymorphs using Kieffer's (1979) methodology. MgGeO<sub>3</sub> clinopyroxene belongs to space group *C2/c*, has four formula units in its primitive unit cell and hence has 60 vibrational degrees of freedom, three of which are acoustic modes. Orthopyroxene belongs to space group *Pbca*, has 16 formula units, and 240 degrees of freedom, three of which are acoustic modes. The spectra of MgGeO<sub>3</sub> orthopyroxene and clinopyroxene (Figs. 2 and 3) show bands extending from 700 to 900 cm<sup>-1</sup> that are commonly assigned to Ge-O stretching motions within the tetrahedral GeO<sub>4</sub> groups (e.g., Tarte, 1962). The bands between 570 and 600 cm<sup>-1</sup> may be attributed to motions of the bridged oxygens within the pyroxene chains. The overall distribution of optic modes in orthopyroxene and clinopyroxene is similar; both have one set of modes at low frequencies between 100 and 600 cm<sup>-1</sup> that is distinct and separate from the high-frequency [GeO<sub>4</sub>] stretching regime between 700 and 900 cm<sup>-1</sup> (Figs. 2 and 3). The lowest-frequency optic modes observed in MgGeO<sub>3</sub> orthopyroxene and clinopyroxene are 107 cm<sup>-1</sup> (Fig. 2) and 121 cm<sup>-1</sup>, respectively. Kieffer-type lattice vibrational models for the two polymorphs are shown in Figures 7A and 7B. The general approach to vibrational modeling is the same as that described earlier (Ross et al., 1986), with each model being consistent with the observed acoustic, crystallographic, and spectroscopic data. The models have at least one continuum spanning the low-frequency modes from 98 cm<sup>-1</sup> (orthopyroxene) and 121 cm<sup>-1</sup> (clinopyroxene) up to 570 cm<sup>-1</sup> (orthopyroxene) and 600 cm<sup>-1</sup> (clinopyroxene) (Fig. 7A, 7B). The top of the longitudinal acoustic branch, which disperses to 98 cm<sup>-1</sup> at the Brillouin zone boundary, was chosen as the low-frequency cutoff for the continuum of MgGeO<sub>3</sub> orthopyroxene since it is unlikely that there is a gap between 98 and 107 cm<sup>-1</sup> (lowest-frequency optic mode observed) in the vibrational density of states. The high-frequency modes between 700 and 900 cm<sup>-1</sup> are represented either with Einstein oscillators or a second continuum (Figs. 7A and 7B). Approximately 25–27% of the optic modes are assigned to this high-frequency region, in keeping with Kieffer's (1980) mode-partitioning scheme for chain silicates and Ross et al.'s (1986) fractionation scheme. Parameters used for converting  $C_V$  to  $C_P$  are given in Table 4. The vibrational models predict that MgGeO<sub>3</sub> orthopyroxene has a greater entropy than

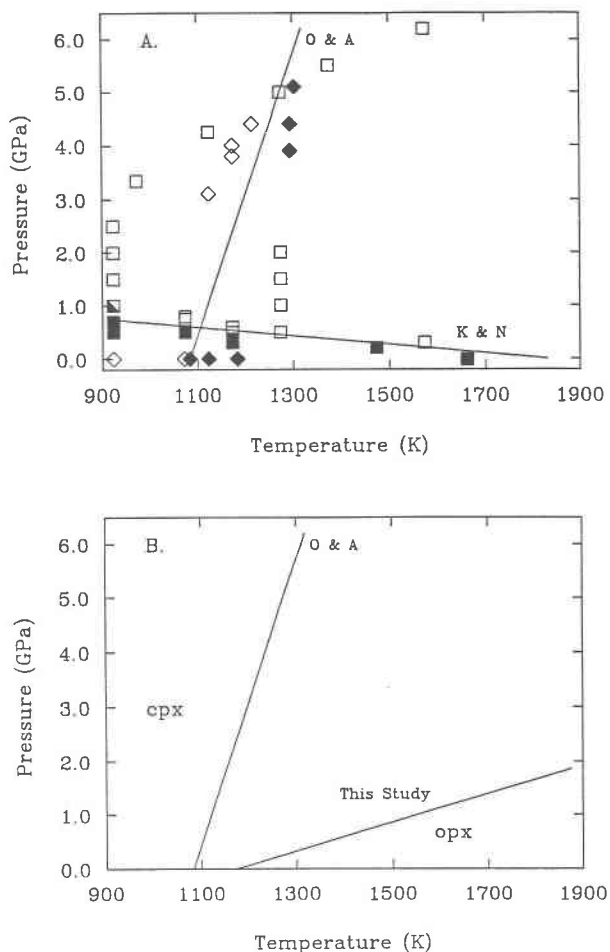


Fig. 5. The MgGeO<sub>3</sub> orthopyroxene-clinopyroxene phase boundary: (A) Experimental data of Kirfel and Neuhaus (1974) (squares) and Ozima and Akimoto (1983) (diamonds). Filled squares and diamonds represent orthopyroxene, and open squares and diamonds represent clinopyroxene. (B) Comparison of the calculated boundary from this study with Ozima and Akimoto's (1983) phase boundary.

clinopyroxene and estimates of  $\Delta S^0$  at 298 and 1000 K range from  $-1.5$  to  $-2.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  (Table 5).

Three major factors contribute to a high vibrational entropy of a crystal (Ross et al., 1986). These are (1) the size of the primitive unit cell, which dictates the contribution from low-frequency acoustic modes, (2) the concentration of the entire optic-mode distribution to low and moderate frequencies found, for example, in highly coordinated phases such as perovskite, and (3) the occurrence of optic modes at low frequencies. Since the overall distribution of optic modes between MgGeO<sub>3</sub> orthopyroxene and clinopyroxene is similar, the difference in entropy between the two phases is due primarily to factors (1) and (3). There is a greater contribution to the entropy from the acoustic modes in MgGeO<sub>3</sub> clinopyroxene; this effect, however, is offset by factor (3), the larger population of optic modes at low frequencies in ortho-

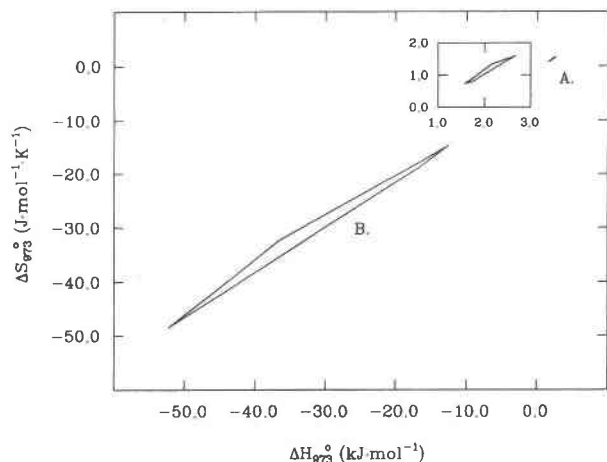


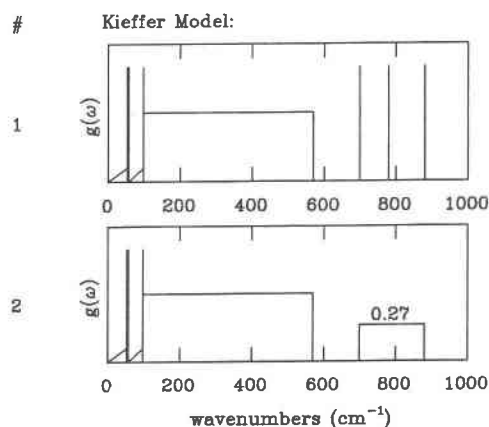
Fig. 6. Results of self-consistency analyses of (A) Kirfel and Neuhaus's (1974) and (B) Ozima and Akimoto's (1983) studies of the MgGeO<sub>3</sub> orthopyroxene-clinopyroxene phase boundary.

pyroxene. The latter is responsible for the higher entropy of MgGeO<sub>3</sub> orthopyroxene relative to MgGeO<sub>3</sub> clinopyroxene.

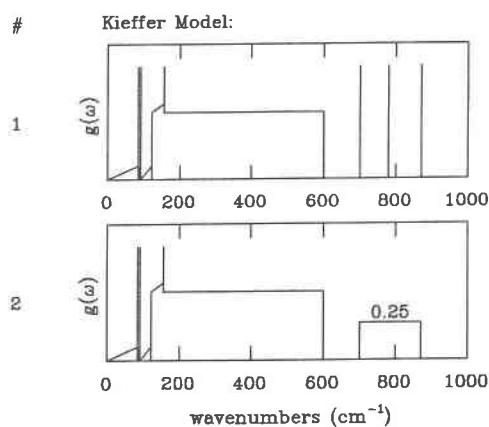
A second estimate of the entropy of transition can be calculated from combining the calorimetric determination of the enthalpy of transition with a known point on the *P-T* boundary. Given that  $\Delta H_{973}^0$  is  $-3440 \pm 661 \text{ J}\cdot\text{mol}^{-1}$  and the transition temperature is between 1123 and 1173 K at 1 atm (Yamanaka et al., 1985), then  $\Delta S^0$  is approximately  $-3.0 \pm 0.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . This value is in good agreement with the value determined from the vibrational models. The greater entropy of MgGeO<sub>3</sub> orthopyroxene (the high-temperature phase), and hence the negative value for  $\Delta S^0$  (opx  $\rightarrow$  cpx), means that the slope of the *P-T* boundary for the transition must be positive, which is consistent with Ozima and Akimoto's (1983) study but not that of Kirfel and Neuhaus (1974). However, although the magnitude of  $\Delta S^0$  is similar to entropies of transition reported for other pyroxene and pyroxenoid phase transitions (Navrotsky, 1981), it is much smaller than the range of  $\Delta S^0$ 's derived from Ozima and Akimoto's (1983) study.

The calculated phase boundary based on the independent determinations of  $\Delta H^0$  from high-temperature solution calorimetry and  $\Delta S^0$  from Kieffer-type lattice vibrational models is compared with Ozima and Akimoto's boundary in Figure 5b. The slope of the calculated boundary,  $0.0021 \text{ GPa}\cdot\text{K}^{-1}$ , is significantly smaller than that determined by Ozima and Akimoto (1983),  $0.0263 \text{ GPa}\cdot\text{K}^{-1}$ . This discrepancy is too large to be explained by systematic errors in the calibration of the high-pressure apparatus used by Ozima and Akimoto (1983). A potential source of error in this study could come from the prediction of  $\Delta S^0$  from the vibrational models. The entropy of transition, and hence  $dP/dT$ , could have been underestimated in the vibrational calculations if a mode below  $98 \text{ cm}^{-1}$  was not included in the models of Mg-

### A. MgGeO<sub>3</sub> Orthopyroxene



### B. MgGeO<sub>3</sub> Clinopyroxene



### C. MgGeO<sub>3</sub> Ilmenite

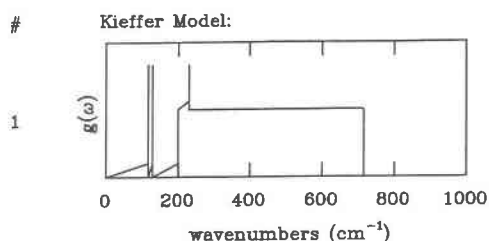


Fig. 7. Kieffer-type lattice vibrational models of (A) MgGeO<sub>3</sub> orthopyroxene, (B) MgGeO<sub>3</sub> clinopyroxene, and (C) MgGeO<sub>3</sub> ilmenite.

GeO<sub>3</sub> orthopyroxene, either because it was too weak to be observed or because it was an inactive mode. Calculation shows that if, for example, a mode at  $60 \text{ cm}^{-1}$  was present in MgGeO<sub>3</sub> orthopyroxene,  $\Delta S_{973}^0$  would increase to  $-11 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $dP/dT$  to  $0.009 \text{ GPa}\cdot\text{K}^{-1}$ . Such an increase would have to be accompanied by an increase in  $\Delta H_{973}^0$  to approximately  $-12,000 \text{ J}\cdot\text{mol}^{-1}$  in order to approach consistency with Ozima and Akimoto's (1983) study (Fig. 6); that is, the calorimetric determination of

**TABLE 4.** Molar volumes, thermal expansion, and bulk modulus data of MgGeO<sub>3</sub> polymorphs

Phase	$V_{298}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\alpha$ ( $\times 10^{-5}$ ·K <sup>-1</sup> )	$K$ (GPa)	$K'$
Orthopyroxene	33.868(5) <sup>A</sup>	4.06(2) <sup>C</sup>	115 <sup>E</sup>	4 <sup>H</sup>
Clinopyroxene	32.695(5) <sup>A</sup>	3.61(28) <sup>C</sup>	115 <sup>F</sup>	4 <sup>H</sup>
Ilmenite	29.091(14) <sup>B</sup>	2.20 <sup>D</sup>	187(2) <sup>G</sup>	4 <sup>H</sup>

Note: Sources indicated by superscript letters. (A) Ozima and Akimoto (1983). (B) Kirfel et al. (1978). (C) Calculated from Yamanaka et al.'s (1985) data. (D) Ashida et al. (1985). (E) Kandelin et al. (unpub. ms.). (F) Assumed to be the same as MgGeO<sub>3</sub> orthopyroxene. (G) Sato et al. (1977); (H) Assumed. Errors given (in parentheses) where available.

$\Delta H_{973}^0$ ,  $-3440 \pm 661$  J·mol<sup>-1</sup>, would have to be in error by  $13\sigma$ , which is unrealistic. Moreover, our low values of  $\Delta S^0$  and  $\Delta H^0$  are consistent with values observed for other pyroxene and pyroxenoid transitions (Navrotsky, 1981). In addition, the second determination of  $\Delta S^0$ ,  $-3.0 \pm 0.6$  J·mol<sup>-1</sup>, shows excellent agreement with the vibrational calculations. In conclusion, we cannot account for the discrepancy between this study and that of Ozima and Akimoto (1983). We would note, however, that some of their reported orthopyroxene to clinopyroxene reversals lie within the stability field of the ilmenite polymorph of MgGeO<sub>3</sub> (see below). Further work, preferably an in situ determination of the orthopyroxene to clinopyroxene phase boundary, is needed.

#### Clinopyroxene to ilmenite transition

At higher pressures, MgGeO<sub>3</sub> clinopyroxene transforms to the ilmenite structure. The results of Kirfel and Neuhaus's (1974) experimental study are shown in Figure 8A. These experiments were synthesis runs using, in most cases, MgGeO<sub>3</sub> orthopyroxene as the starting material, and the  $P$ - $T$  boundary was found to be  $P$  (in GPa) =  $-1.80 + 0.0056 T$  (in K). Self-consistency analysis of their data set shows that the data are internally consistent and gives values of  $\Delta H^0$  and  $\Delta S^0$  from 13800 to 2090 J·mol<sup>-1</sup> and from  $-12.5$  to  $-27.2$  J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively (Fig. 9). Parameters used in the self-consistency analysis are given in Table 4.

Since Kirfel and Neuhaus's (1974) experiments are predominantly synthesis runs, independent determinations of  $\Delta H^0$  and  $\Delta S^0$  provide valuable crosschecks on the high-pressure experiments. The enthalpy of this transition calculated from the heat of solution data (Table 1) is  $7808 \pm 561$  J·mol<sup>-1</sup>. This value is much greater than those found to be consistent with Kirfel and Neuhaus's (1974) experimental data (Fig. 9). An independent determination of  $\Delta S^0$  can be obtained from Kieffer-type lattice vibrational models of the two polymorphs. The vibrational models for MgGeO<sub>3</sub> clinopyroxene (Fig. 7B) are characterized by two separate optic continua or one continuum and a set of Einstein oscillators that span the two regions where the bulk of the vibrational modes occur, between 121 and 600 cm<sup>-1</sup> and at higher frequencies between 700 and 900 cm<sup>-1</sup> (Fig. 3). In addition, the acoustic modes represent 5% of the total vibrational modes. MgGeO<sub>3</sub> ilmenite, on the other hand, belongs to space group  $R\bar{3}$ ,

**TABLE 5.** Heat capacities and entropies calculated from vibrational models (shown in Fig. 7)

Model	$T$ (K)	$C_p$ (J·mol <sup>-1</sup> )	$S^0$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
<b>A. MgGeO<sub>3</sub> orthopyroxene</b>			
1	298	87.88	77.00
	700	121.03	168.18
	1000	128.10	212.68
2	298	87.68	76.86
	700	120.96	167.92
	1000	128.06	212.41
<b>B. MgGeO<sub>3</sub> clinopyroxene</b>			
1	298	86.92	75.41
	700	119.92	165.77
	1000	126.61	209.82
2	298	87.19	75.53
	700	120.08	166.10
	1000	126.70	210.18
<b>C. MgGeO<sub>3</sub> ilmenite</b>			
1	298	87.52	69.54
	700	117.64	159.46
	1000	122.81	202.42

has two formula units in its primitive unit cell, and hence has 30 vibrational degrees of freedom. Thus, the acoustic modes represent 10% of the total number of vibrational modes. The Raman and infrared spectra of MgGeO<sub>3</sub> ilmenite (Fig. 4) show that the bulk of the vibrational modes are distributed uniformly between 204 and 722 cm<sup>-1</sup>. Because Mg and Ge are both in octahedral coordination in the ilmenite structure, there are no high-frequency modes above 722 cm<sup>-1</sup> and no noticeable breaks in the frequency distribution of the ilmenite spectra. The most appropriate vibrational model (Fig. 7C) is therefore a simple one consisting of a single optic continuum spanning this range of frequencies. The heat capacities predicted from this model (Table 5) show excellent agreement with Ashida et al.'s (1985) data (Fig. 10). The entropy of transition at 1000 K for MgGeO<sub>3</sub> clinopyroxene to ilmenite, based on a number of vibrational models, is  $-7.6 \pm 1.5$  J·mol<sup>-1</sup>·K<sup>-1</sup>. MgGeO<sub>3</sub> clinopyroxene has the greater entropy because the presence of modes at low frequencies, extending to 121 cm<sup>-1</sup>, outweighs both the contribution to the entropy from the acoustic modes and from the concentration of modes below 722 cm<sup>-1</sup> that are found in MgGeO<sub>3</sub> ilmenite. The latter, however, are responsible for the value of the entropy of transition being less negative than one might expect. The value of  $\Delta S^0$ , in fact, determined from these models is much lower than the values found to be consistent with Kirfel and Neuhaus's (1974) study (Fig. 9).

In the past, studies on the Mg<sub>2</sub>SiO<sub>4</sub> polymorphs (Akaogi et al., 1984), the CaGeO<sub>3</sub> polymorphs (Ross et al., 1986), and the Mg<sub>2</sub>GeO<sub>4</sub> polymorphs (Ross and Navrotsky, 1987) have successfully constrained thermodynamic parameters of phase transitions by combining the phase studies with independent determinations of  $\Delta H^0$  and  $\Delta S^0$  from calorimetric and lattice vibrational calculations. The MgGeO<sub>3</sub> clinopyroxene to ilmenite transition is remarkable in that independent determinations of  $\Delta H^0$  and  $\Delta S^0$  are inconsistent with Kirfel and Neuhaus's (1974) study. In order to resolve these discrepancies, we re-examined



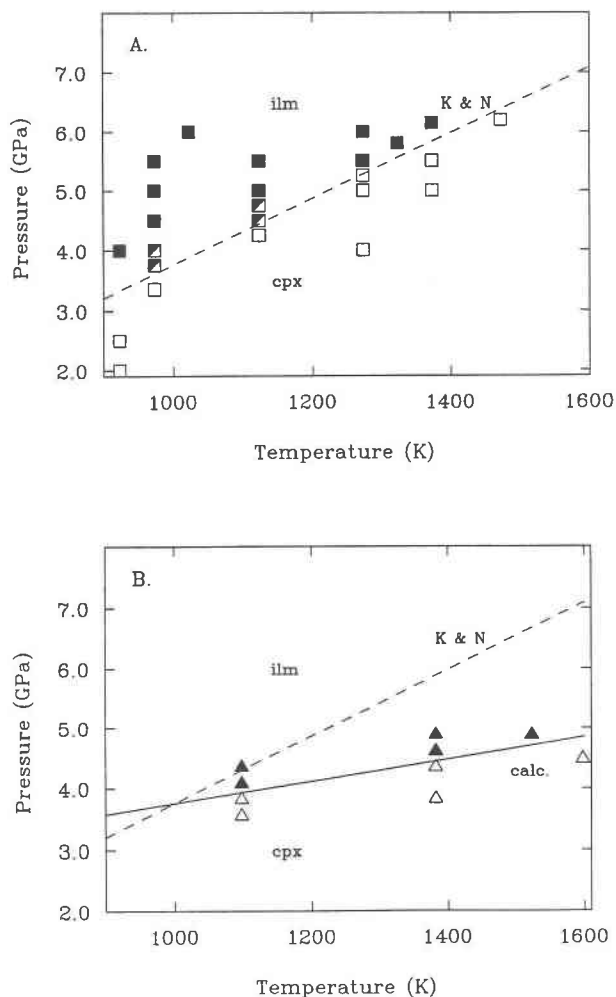


Fig. 8. The MgGeO<sub>3</sub> clinopyroxene-ilmenite boundary: Experimental data of (A) Kirfel and Neuhaus (1974) and (B) this study. The calculated boundary based on the calorimetric data and vibrational calculations is shown as a solid line in (B).

this transition with reversal experiments at high pressures and temperatures (Fig. 8B). A self-consistency analysis of the new experimental data defines a set of enthalpies and entropies of transition that range from 1918 to 9368 J·mol<sup>-1</sup> and from -5.8 to -11.7 J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively (Fig. 9). The calorimetric determinations of  $\Delta H_{973}^0$ , 7808 ± 561 J·mol<sup>-1</sup>, and  $\Delta S_{973}^0$  estimated from lattice vibrational models, -7.6 ± 1.5 J·mol<sup>-1</sup>·K<sup>-1</sup>, both lie within the set of values consistent with the new phase-equilibrium study (Fig. 9). The most striking difference between this phase boundary,  $P$  (in GPa) = 1.913 + 0.0018  $T$  (in K), and that of Kirfel and Neuhaus (1974),  $P$  (in GPa) = -1.80 + 0.0056  $T$  (in K), is its much shallower slope (Fig. 8b).

In conclusion, thermodynamic parameters for the MgGeO<sub>3</sub> clinopyroxene to ilmenite transition have been tightly constrained from a combination of high-temperature solution calorimetric experiments, lattice vibrational calculations, and phase-equilibria experiments. The

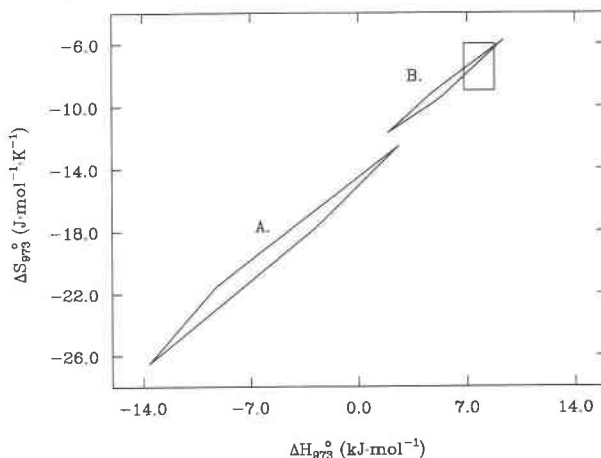


Fig. 9. Results from the self-consistency analyses of (A) Kirfel and Neuhaus's (1974) and (B) this study's experimental data for MgGeO<sub>3</sub> clinopyroxene-ilmenite. The box outlines the values, including error bars, of  $\Delta H_{973}^0$  determined from calorimetry and  $\Delta S_{973}^0$  calculated from Kieffer-type vibrational models.

values of  $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta V^0$  for this transition are 7808 ± 561 J·mol<sup>-1</sup>, -7.6 ± 1.5 J·mol<sup>-1</sup>·K<sup>-1</sup>, and -3.61 cm<sup>3</sup>·mol<sup>-1</sup>, respectively. This study shows that caution must be exercised when extracting thermodynamic parameters from phase studies in which the runs are synthesis rather than reversal experiments.

## DISCUSSION

It is interesting to compare the present thermochemical data for the MgGeO<sub>3</sub> polymorphs with those of the CdGeO<sub>3</sub> polymorphs (Table 6). At 1 atm, CdGeO<sub>3</sub> adopts a pyroxenoid structure rather than a pyroxene structure because the former can accommodate larger octahedral cations more easily than the pyroxene structure. With increasing pressure, CdGeO<sub>3</sub> pyroxenoid transforms first to a garnet structure, then to an ilmenite structure, and finally to a perovskite structure (Susaki and Akimoto, 1983). There is a suggestion that MgGeO<sub>3</sub> transforms to the perovskite structure under some high-pressure and high-temperature conditions (Liu and Bassett, 1986). Thus the sequence of transitions in MgGeO<sub>3</sub> is similar to those in CdGeO<sub>3</sub> except that MgGeO<sub>3</sub> has no garnet stability field. The enthalpy, entropy, and volume changes for the CdGeO<sub>3</sub> pyroxenoid-ilmenite transition (Table 6) have been calculated from the data for the pyroxenoid-garnet and garnet-ilmenite transitions (Akaogi and Navrotsky, 1987). The thermochemical data for CdGeO<sub>3</sub> presented by Akaogi and Navrotsky (1987) show reasonably good agreement with phase studies of Susaki and Akimoto (1983). The pyroxene (or pyroxenoid) to ilmenite transition involves a large structural change from a structure with chains of corner-linked [GeO<sub>4</sub>] tetrahedra cross-linked by M (M = Mg, Cd) cations in octahedral coordination to a structure with alternating layers of [MO<sub>6</sub>] and [GeO<sub>6</sub>] octahedra that share edges within the layers and faces between the layers. Consequently, a large volume decrease is associated with this transition; the volume

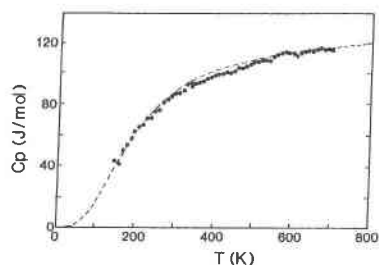


Fig. 10. Comparison of calculated heat capacities of MgGeO<sub>3</sub> ilmenite as a function of temperature from the vibrational model (dashed curve) with experimental data from Ashida et al. (1985) (solid circles).

changes in MgGeO<sub>3</sub> and CdGeO<sub>3</sub> are  $-3.61 \text{ cm}^3 \cdot \text{mol}^{-1}$  (11%) and  $-7.06 \text{ cm}^3 \cdot \text{mol}^{-1}$  (17%), respectively. One might expect such a transition to be energetically very costly, but both MgGeO<sub>3</sub> and CdGeO<sub>3</sub> have moderate, positive enthalpies of transition, 7808 and 9271 J·mol<sup>-1</sup>, respectively. The entropies of the pyroxene (pyroxenoid)-ilmenite transition are also similar. MgGeO<sub>3</sub> has a  $\Delta S^0$  of  $-7.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  and CdGeO<sub>3</sub> has a  $\Delta S^0$  of  $-9.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . Thus  $dP/dT$  for the metastable CdGeO<sub>3</sub> pyroxenoid-ilmenite transition would be positive, similar to  $dP/dT$  for MgGeO<sub>3</sub> pyroxene-ilmenite (Table 6).

In the introduction, we noted that germanates are often used as geochemical models for silicates. Previous studies of the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene phase transition have been undertaken in order to elucidate the nature of the orthoenstatite to low clinoenstatite transition in MgSiO<sub>3</sub>. The analogy, however, is not a good one because low clinoenstatite differs structurally from MgGeO<sub>3</sub> clinopyroxene and belongs to space group  $P2_1/c$ , not  $C2/c$ . The difference in volume between low clinoenstatite and orthoenstatite is  $-0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$ , two orders of magnitude smaller than  $\Delta V^0$  for the orthopyroxene to clinopyroxene transition in MgGeO<sub>3</sub>,  $-1.173 \text{ cm}^3 \cdot \text{mol}^{-1}$ . Moreover, the enthalpy and entropy of transition for MgSiO<sub>3</sub> (opx → cpx) are substantially smaller than those determined for MgGeO<sub>3</sub> in this study. The enthalpy of transition for MgSiO<sub>3</sub> (opx → cpx), for example, is 167 J·mol<sup>-1</sup> (Navrotsky, 1981) compared to  $-3440 \text{ J} \cdot \text{mol}^{-1}$  for MgGeO<sub>3</sub>. The entropy of transition is essentially zero in MgSiO<sub>3</sub> (Navrotsky, 1981) as compared to  $-3.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  in MgGeO<sub>3</sub>. Recently, however, Pacalo and Gasparik (1987) have reported reversals of a phase boundary at pressures and temperatures exceeding 6.0 GPa and 1173 K between orthoenstatite and a high-pressure polymorph of MgSiO<sub>3</sub> that is possibly a  $C2/c$  high clinoenstatite phase. The slope of their phase boundary,  $0.0034 \text{ GPa} \cdot \text{K}^{-1}$  (Gasparik, pers. comm.), is very similar to that of the MgGeO<sub>3</sub> orthopyroxene to clinopyroxene transition,  $0.0026 \pm 0.0013 \text{ GPa} \cdot \text{K}^{-1}$ , determined in this study. These findings indicate that MgGeO<sub>3</sub> orthopyroxene and clinopyroxene may provide better analogues for this high-pressure transition in MgSiO<sub>3</sub>, than for the orthoenstatite to low clinoenstatite

TABLE 6. Thermochemical data for pyroxene (or pyroxenoid)-ilmenite transition in MgGeO<sub>3</sub> and CdGeO<sub>3</sub>

Compound	$\Delta H^0$ (J·mol <sup>-1</sup> )	$\Delta S^0$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta V^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$dP/dT$ (×10 <sup>-3</sup> GPa·K <sup>-1</sup> )	Ref.*
MgGeO <sub>3</sub>	7808 ± 562	-7.6 ± 1.5	-3.61	2.0 ± 0.4	a
CdGeO <sub>3</sub>	9271 ± 1683	-9.7 ± 3.7	-7.06	1.4 ± 0.5	b

\* a = this study; b = Akaogi and Navrotsky (1987).

transition. Additional data on silicate pyroxenes at high pressures and temperatures will enhance our overall understanding of the pressure, temperature, and composition relations of the pyroxene polymorphs.

#### ACKNOWLEDGMENTS

Our sincere thanks go to S. Kume of Osaka University, Japan, who provided the inspiration for this project. A. Hofmeister and R. Hemley are gratefully acknowledged for their help with the spectroscopy. C. T. Prewitt is thanked for supporting N.L.R. with NSF grant EAR-8618602. All calorimetric experiments were performed in A.N.'s laboratory at Princeton University, which is supported by NSF grant DMR 86-10816. The high-pressure experiments reported in this paper were performed in the Stony Brook High Pressure Laboratory, which is jointly supported by the National Science Foundation Division of Earth Sciences (86-07105) and the State University of New York at Stony Brook.

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MANUSCRIPT RECEIVED FEBRUARY 16, 1988

MANUSCRIPT ACCEPTED AUGUST 1, 1988