

## Heat capacities and entropies of $\text{Mg}_2\text{SiO}_4$ , $\text{Mn}_2\text{SiO}_4$ , and $\text{Co}_2\text{SiO}_4$ between 5 and 380 K

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### Abstract

The heat capacities of synthetic single crystals of  $\text{Mg}_2\text{SiO}_4$  (forsterite),  $\text{Mn}_2\text{SiO}_4$  (tephroite), and  $\text{Co}_2\text{SiO}_4$  (cobalt olivine), were measured between 5 and 380 K using an adiabatically shielded calorimeter.  $\text{Mg}_2\text{SiO}_4$  is diamagnetic, and its heat capacity follows a normal sigmoidal curve at low temperatures.  $\text{Co}_2\text{SiO}_4$  shows a single sharp  $\lambda$ -type transition at  $49.85 \pm 0.02$  K associated with the antiferromagnetic ordering of the magnetic moments of the  $\text{Co}^{2+}$  ions into a collinear spin arrangement below 49.8 K. In contrast to  $\text{Co}_2\text{SiO}_4$ ,  $\text{Mn}_2\text{SiO}_4$  has two transitions in  $C_p^\circ$ , a sharp  $\lambda$ -type transition at  $47.38 \pm 0.05$  K and a smaller "shoulder" in  $C_p^\circ$  centered near 12 K. The upper transition corresponds to the paramagnetic (disordered) to collinear antiferromagnetic ordering of the  $\text{Mn}^{2+}$  moments, whereas the shoulder near 12 K corresponds to the change from the collinear to a canted spin structure. Our calorimetric values for the antiferromagnetic-paramagnetic transition temperature (Néel Temperature) are in excellent agreement with those obtained by powder magnetic susceptibility measurements,  $49 \pm 2$  K and  $50 \pm 5$  K for  $\text{Co}_2\text{SiO}_4$  and  $\text{Mn}_2\text{SiO}_4$  respectively.

The thermal Debye temperature,  $\theta_D^C$ , of  $\text{Mg}_2\text{SiO}_4$  calculated from our  $C_p^\circ$  measurements between 6.3 and 13.8 K is  $768 \pm 15$  K and agrees well with the elastic value  $\theta_D^E$  of 758 K based on the mean sound velocity calculated from the room temperature elastic stiffness constants ( $c_{ij}$ ) of Graham and Barsch.

At 298.15 K (25°C) the molar heat capacities are 118.6, 128.7, and 133.4 J/(mol · K) and the molar entropies are  $94.11 \pm 0.10$ ,  $155.9 \pm 0.4$  and  $142.6 \pm 0.2$  J/(mol · K) respectively for  $\text{Mg}_2\text{SiO}_4$ ,  $\text{Mn}_2\text{SiO}_4$ , and  $\text{Co}_2\text{SiO}_4$ .

### Introduction

The olivine group minerals are one of the more important constituents of igneous rocks and are believed to be a dominant phase in the upper mantle of the earth. They are also significant as the precursor minerals from which certain commercial talc and asbestos deposits have formed. Accurate values for their thermodynamic properties over a wide temperature range are thus necessary for the quantitative solution of both geochemical and geophysical problems.

The olivines have the general formula  $\text{M}_2(\text{SiO}_4)$  where M is Mg, Fe, Mn, Ni, Ca, and Co. They crystallize in the orthorhombic space group  $Pbnm$  (62) with 4 formulas per unit cell.  $\gamma\text{-Ca}_2\text{SiO}_4$  (calcio-

olivine) occurs very rarely in nature and  $\text{Co}_2\text{SiO}_4$  does not occur as a discrete mineral. However, studies by Ross and others (1954) indicate that Co and Ca are common, though minor components in many olivines, and  $\gamma\text{-Ca}_2\text{SiO}_4$  is important in the phase chemistry of Portland cement clinker.

The crystal structure of the olivine form of  $\text{Mg}_2\text{SiO}_4$  has been refined by Hazen (1976) and that of  $\text{Co}_2\text{SiO}_4$  by Morimoto *et al.* (1974). Fujino *et al.* (1981) have refined the structures of synthetic forsterite and tephroite prepared by one of us (H.T.).

The olivine structure is based on a slightly distorted hexagonal close-packed array of oxygen atoms in which one-eighth of the tetrahedral interstices are filled by silicon and one-half of the octahedral interstices are occupied by the divalent

cation M. The divalent cations occupy two crystallographically distinct sites normally called M(1) and M(2). The M(1) site has the point symmetry  $\bar{1}$  whereas M(2) has point symmetry  $m$ .

Powder neutron diffraction studies by Nomura *et al.* (1964) indicate that in  $Co_2SiO_4$  the spins associated with the  $Co^{2+}$  ions are collinearly ordered parallel to [001] at temperatures below 49 K. Similar studies by Santoro *et al.* (1966) show that tephroite has a canted antiferromagnetic spin structure below 13 K, and has the same collinearly ordered spin structure as  $Co_2SiO_4$  between 13 and 47.4 K.

Previous studies of the low-temperature heat capacities of  $Mg_2SiO_4$  were made by Kelley (1943) over the temperature range 53.2–295.0 K. King and Weller (reported by Mah, 1960) measured  $C_p^o$  of  $Mn_2SiO_4$  between 52.3 and 296.1 K. Orr (1953) has measured the heat content of  $Mg_2SiO_4$  between 298 and 1800 K and Christiansen (reported by Mah, 1960) has determined  $H_T^o - H_{298}^o$  up to 1795 K for crystals and liquid  $Mn_2SiO_4$ . We are unaware of any previous measurements on the heat capacity or heat content of cobalt olivine.

### Materials

#### $Mg_2SiO_4$

The forsterite sample was a single crystal boule grown by the Czochralski method using an iridium crucible. The starting materials were 99.9 percent purity MgO and  $SiO_2$  which were blended in the 2:1 molar proportions and sintered in a resistance furnace for 6 hours at 1300°C. The crystal was pulled from the molten  $Mg_2SiO_4$  ( $\approx 1900^\circ C$ ) at 3 to 10 mm/hour with a rotation rate of 20 to 30 revolutions/min under a nitrogen atmosphere (flow rate 1–3 liter/min). Details of the apparatus and growth procedures are given by Takei and Kobayashi (1974) who also provide chemical analyses, unit cell parameters and densities of several other boules grown under the same conditions. The boule initially was 2.2 cm in diameter with a length of 5.6 cm. In order to fit into our calorimeter it was sliced into quarters, with a diamond saw, parallel to the long axis.

Electron microprobe analyses of our sample by L. B. Wiggins (U.S. Geological Survey) are given in columns 2 and 3 of Table 1. The tabulated values are the averages of 7 and 6 separate analyses respectively.

#### $Mn_2SiO_4$

The tephroite sample was also a single crystal boule, initially 1.7 cm maximum diameter by 5.7 cm

in length. The starting materials were 99.9 percent  $MnCO_3$  and  $SiO_2$  reagents mixed in the 2:1 molar ratio and fired at 1000°C under a nitrogen atmosphere for several hours. The boule was grown from the melt ( $\approx 1350^\circ C$ ) in an iridium crucible under a protective atmosphere of nitrogen plus hydrogen (500:1 by volume) using the Czochralski technique. The pulling rate was 3 to 8 mm/hour with a rotation rate of 10 to 15 revolutions per minute. Additional details of the growth procedure and chemical analyses, X-ray cell parameters, and optical absorption spectra for crystals grown under the same conditions with the same apparatus are given by Takei (1976). Microprobe analyses of the heat capacity sample are listed in columns 5 and 6 of Table 1 and are the averages of 8 and 3 separate analyses respectively.

#### $Co_2SiO_4$

The cobalt orthosilicate sample was composed of fragments of 3 separate boules. The fragments weighed between 3 and 10 grams. The crystals were grown by the floating zone method using the apparatus and techniques described by Takei (1978). Electron probe analyses of the cobalt orthosilicate sample are listed in columns 8 and 9 of Table 1.

### Experimental measurements

The heat capacity measurements were made using the intermittent heating method under quasi-adiabatic conditions using the cryostat described by

Table 1. Chemical analyses of  $Mg_2SiO_4$ ,  $Mn_2SiO_4$  and  $Co_2SiO_4$  single crystals used for heat capacity measurements.

	1	2	3	4	5	6	7	8	9
$SiO_2$	42.71	42.11	42.26	29.75	29.30	29.41	28.62	27.3	27.4
MgO	57.29	58.31	57.05						
MnO				70.25	69.86	70.44			
CoO							71.38	71.8	72.1
	100.00	100.42	99.30	100.00	99.16	99.84	100.00	99.1	99.5
1	$Mg_2SiO_4$								
2, 3	Microprobe analysis by L.B. Wiggins, U.S. Geological Survey								
4	$Mn_2SiO_4$								
5, 6	Microprobe analysis by L.B. Wiggins, U.S. Geological Survey, Reston, VA								
7	$Co_2SiO_4$								
8, 9	Microprobe analysis by L.B. Wiggins, U.S. Geological Survey, Reston, VA								

Robie and Hemingway (1972); together with the calorimeter and semiautomatic data acquisition system described by Robie *et al.* (1976). Temperatures were determined with a Minco model S 1059-1 platinum resistance thermometer ( $R_0 = 100.02$  ohms) which had been calibrated by the Temperature Measurements Section of the National Bureau of Standards on the International Practical Temperature Scale of 1968 (IPTS-68) between 13.8 and 505 K, and the provisional temperature scale used in this laboratory between 4.2 and 13.8 K as discussed by Robie, *et al.* (1978). The samples were sealed in the calorimeter under pure helium gas at a pressure of 5 kPa, (approximately  $4 \times 10^{-5}$  mol of He).

The formula weights used were based on the 1975 values for the atomic weights and are 140.694, 201.960, and 209.950 g mol<sup>-1</sup> for  $Mg_2SiO_4$ ,  $Mn_2SiO_4$ , and  $Co_2SiO_4$  respectively. The sample weights, corrected for buoyancy, used in our measurements were 46.537, 41.200 and 46.012 grams for  $Mg_2SiO_4$ ,  $Mn_2SiO_4$ , and  $Co_2SiO_4$  respectively.

For the measurements on  $Mg_2SiO_4$  the calorimeter contributed 88 percent of the total measured heat capacity at 10 K, 60 percent at 100 K and 43 percent at 300 K and above. For  $Mn_2SiO_4$  the calorimeter contributed approximately 53 percent to the measured heat capacity between 60 and 380 K, dropping to 28 percent at 25 and 5 percent at 10 K. For the measurements on  $Co_2SiO_4$  the calorimeter was 60 percent at 10 K, 38 percent at 50 K and averaged 55 percent between 50 and 380 K. The corrections for deviations from true adiabatic conditions were less than 0.2 percent above 30 K and less than 0.1 percent between 35 and 250 K except for the measurements made with small temperature increments ( $\Delta T < 0.5$  K) in the neighborhood of the antiferromagnetic transitions.

$Mg_2SiO_4$  is diamagnetic and its heat capacity follows a normal sigmoidal curve at low temperatures.  $Co_2SiO_4$  and  $Mn_2SiO_4$  are both paramagnetic and as was anticipated show a sharp  $\lambda$ -type transition in  $C_p^0$  arising from the antiferromagnetic ordering of the  $Co^{2+}$  and  $Mn^{2+}$  spins at low temperatures. In addition,  $Mn_2SiO_4$  exhibits a second, rounded, maxima (shoulder) in  $C_p^0$  near 12 K which, on the basis of the neutron diffraction studies of Santoro *et al.* (1966), we believe is related to the change from a collinearly ordered antiferromagnetic spin arrangement to a canted arrangement of the spins with decreasing temperature.

Our experimental results are listed in Tables 2–4

Table 2. Experimental molar heat capacity measurements on synthetic single crystals of  $Mg_2SiO_4$  (forsterite).

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(g·K)	K	J/(g·K)	K	J/(g·K)
Series 1		Series 5		Series 8	
299.45	0.8451	133.64	0.3741	270.34	0.7885
304.80	0.8552	139.17	0.3967	276.20	0.8005
310.61	0.8651	144.73	0.4189	282.08	0.8124
316.37	0.8751	150.28	0.4405	287.71	0.8234
322.09	0.8839	155.65	0.4609	293.46	0.8343
327.77	0.8935	161.00	0.4808	299.14	0.8444
333.56	0.9024	166.55	0.5008		
		172.15	0.5207	Series 9	
		177.63	0.5395	7.66	0.000018
Series 2		Series 6		9.14	0.000149
335.44	0.9053	175.31	0.5315	10.10	0.000215
341.31	0.9134	180.79	0.5499	11.11	0.000306
346.97	0.9224	186.41	0.5685	12.35	0.000401
Series 3		192.02	0.5862	13.82	0.000578
351.06	0.9259	197.73	0.6039	15.47	0.000830
355.20	0.9324	203.46	0.6211	17.22	0.001004
360.95	0.9407	209.08	0.6375	19.18	0.001698
367.13	0.9494			21.46	0.002463
373.75	0.9575	Series 7		23.71	0.003402
380.31	0.9654	207.86	0.6338	25.85	0.004524
Series 4		213.42	0.6495	Series 10	
52.87	0.04915	219.11	0.6655	6.23	0.000037
58.53	0.06511	224.92	0.6811	7.56	0.000086
63.54	0.08114	230.62	0.6961	8.44	0.000117
68.82	0.09976	236.40	0.7107	Series 11	
74.21	0.1203	242.25	0.7249	26.04	0.004621
79.63	0.1421	248.01	0.7389	28.68	0.006425
85.16	0.1652	253.84	0.7527	31.43	0.008845
90.77	0.1892	259.74	0.7662	34.70	0.01244
96.41	0.2137	265.56	0.7783	38.25	0.01732
101.99	0.2380			41.85	0.02330
107.50	0.2622			45.88	0.03133
112.83	0.2854			50.12	0.04158
118.02	0.3080				
123.10	0.3298				
128.25	0.3516				

in their chronological order of measurement. The heat capacities of  $Mg_2SiO_4$  and  $Co_2SiO_4$  are shown in Figure 1 and those of  $Mn_2SiO_4$  in Figure 2.

For  $Mn_2SiO_4$  and  $Co_2SiO_4$  we made replicate measurements in the region of the  $C_p^0$  anomalies using temperature increments of 0.3–0.18 K in order to delineate the exact form of the heat capacity in the transition regions. These are shown in Figures 3 and 4 for  $Co_2SiO_4$  and  $Mn_2SiO_4$  respectively.

#### Thermodynamic properties of $Mg_2SiO_4$ , $Mn_2SiO_4$ , and $Co_2SiO_4$

Our experimental heat capacities were graphically extrapolated to 0 K using a plot of  $C_p^0/T$  versus  $T^2$  as shown in Figure 5.

Above 30 K the heat capacity data were analytically smoothed using an orthogonal polynomial

Table 3. Experimental molar heat capacity measurements on synthetic single crystals of  $Mn_2SiO_4$  (tephroite).

Temp K	Heat Capacity J/(mol·K)	Temp K	Heat Capacity J/(mol·K)
Series I			
303.63	129.8		
309.63	131.1		
315.36	132.2		
321.05	133.3		
326.69	134.4		
Series II			
326.48	134.4		
332.30	135.7		
338.57	136.8		
344.78	137.6		
350.94	138.7		
357.16	139.7		
363.43	140.7		
369.65	141.7		
375.84	142.6		
381.99	143.3		
Series III			
51.72	29.83		
52.99	30.99		
60.04	32.60		
Series IV			
65.18	34.69		
70.06	37.31		
74.97	40.23		
Series V			
74.12	42.14		
83.42	45.49		
88.67	48.58		
94.22	51.96		
Series VI			
93.79	45.58		
93.79	48.69		
93.96	51.82		
93.60	55.19		
Series VII			
100.39	55.66		
106.06	58.97		
111.53	62.08		
117.19	65.24		
122.92	68.37		
128.52	71.32		
134.02	74.13		
139.35	75.75		
144.73	79.37		
150.17	91.91		
155.67	84.38		
Series VIII			
161.29	86.84		
167.17	89.32		
172.98	91.77		
178.87	94.17		
184.83	96.44		
190.75	98.54		
Series IX			
196.52	100.7		
202.32	102.7		
208.18	104.7		
214.03	106.6		

\*Mean heat capacity between 44.31 and 48.72 K.

Table 4. Experimental molar heat capacity measurements on single crystals of  $Co_2SiO_4$  (olivine structure).

Temp K	Heat Capacity J/(mol·K)	Temp K	Heat Capacity J/(mol·K)
Series I			
309.16	135.8	194.71	102.6
315.00	137.1	200.38	104.7
320.82	138.3	206.07	106.8
326.08	139.5	211.76	108.8
332.55	140.7	217.47	110.7
338.48	141.9	223.21	112.6
Series II			
344.32	143.1	228.82	114.5
350.22	144.2	234.50	116.2
356.19	145.3	240.26	118.0
362.24	146.4	246.01	119.7
368.37	147.4		
374.57	148.5		
380.83	149.5		
Series III			
50.12	32.77	251.20	121.2
51.02	27.67	257.18	123.0
52.10	26.62	263.04	124.6
53.17	26.21	268.85	126.2
54.23	26.30	274.59	127.7
55.25	26.51	280.25	129.2
58.13	27.65	285.90	130.6
62.97	30.27	291.50	132.0
67.90	33.39	297.06	133.1
72.92	36.77		
77.97	40.27		
83.05	43.83		
88.21	47.37		
Series IV			
88.63	47.67		
94.10	51.34	7.53	.0236
99.36	54.91	9.57	.0825
104.60	58.16	10.61	.1295
109.96	61.50	11.64	.1902
115.54	64.89	12.89	.2933
121.25	68.26	14.38	.4813
126.87	71.45	16.13	.7989
Series V			
132.52	74.57	18.06	1.302
138.28	77.64	20.07	2.023
143.82	80.43	22.41	3.088
149.40	83.16	24.94	4.566
155.02	85.85	27.45	6.359
160.78	88.53	30.08	8.627
166.66	91.16	32.91	11.58
Series VI			
172.37	93.62	35.95	15.39
177.95	95.98	39.41	20.67
183.61	98.30	43.28	28.55
189.35	100.6		
Series VII			
		5.76	.0081
		6.76	.0182
		7.51	.0288
		8.46	.0513
		9.65	.0880
		10.78	.1380
Series VIII			
		46.05	36.48
		47.69	43.40
		48.08	45.71
		48.32	47.21
		48.54	48.92
		48.76	50.84
		48.97	53.15
		49.17	55.80
		49.37	59.31
		49.55	64.05
		49.73	64.04*
		49.95	39.47

\*Mean heat capacity between 49.64 and 49.82 K.

curve fitting routine (except in the transition regions). The analytically and graphically smoothed parts were joined smoothly and corrected for curvature. Our measurements for  $Mg_2SiO_4$  have an average deviation from the smoothed curve of  $\pm 0.06$  percent between 25 and 380 K and maximum deviations of 0.5 percent.

From replicate measurements on all three samples in the range 5 to 10 K together with our

previous (unpublished) data on the Calorimetry Conference Copper sample (Osborne, Flotow, and Schreiner, 1967) between 4.5 and 20 K, we believe that our smoothed  $C_p$  values are accurate to approximately  $\pm 5$  percent between 5 and 15 K, increasing in accuracy to  $\pm 0.1$  percent for temperatures above 20 K except in the immediate region of  $T_N$  where the small temperature increments reduced the accuracy to  $\pm 1.0$  percent.

Smooth values for the thermodynamic functions  $C_p$ ,  $S_T^0 - S_0^0$ ,  $(H_T^0 - H_0^0)/T$ , and  $(G_T^0 - H_0^0)/T$  for  $Mg_2SiO_4$ ,

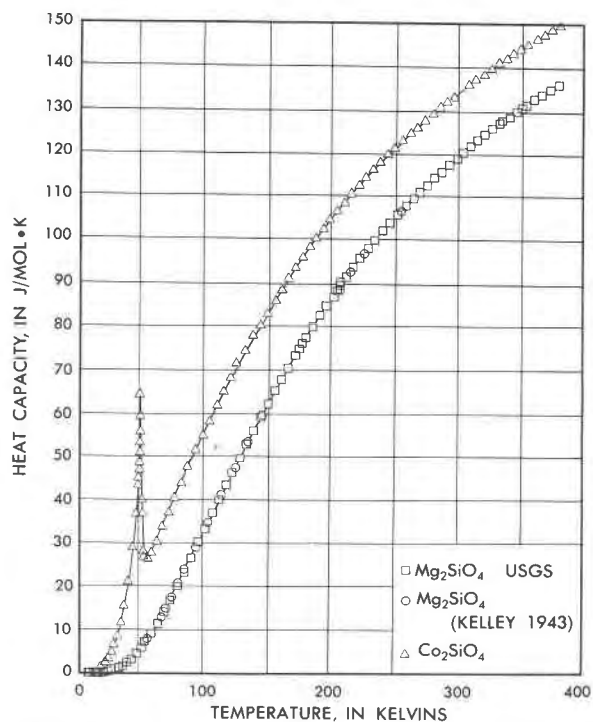


Fig. 1. Experimental molar heat capacity of synthetic single crystal  $Mg_2SiO_4$  (forsterite), formula weight  $140.694 \text{ g mol}^{-1}$  and synthetic single crystal  $Co_2SiO_4$  formula weight  $209.950 \text{ g mol}^{-1}$ . Earlier measurements of Kelley (1943) on powdered  $Mg_2SiO_4$  between 53.2 and 295.0 K are shown for comparison.

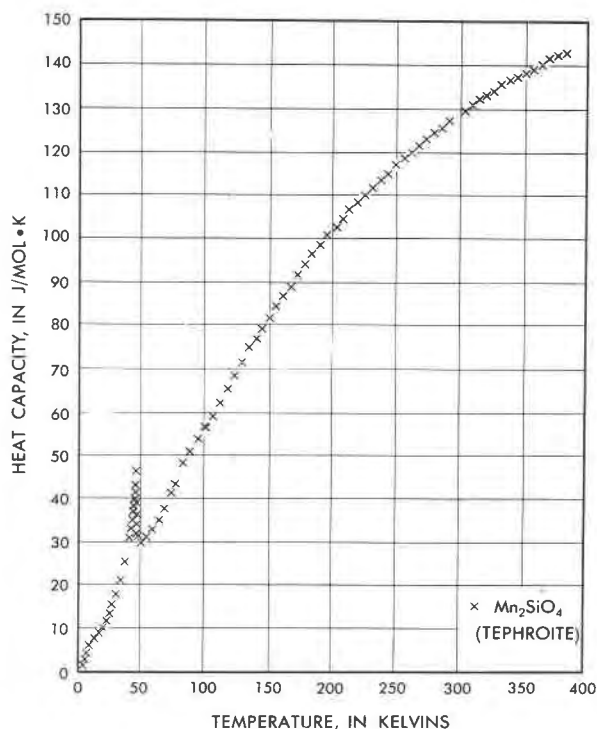


Fig. 2. Experimental molar heat capacities of synthetic single crystal  $Mn_2SiO_4$  (tephroite), formula weight =  $201.960 \text{ g mol}^{-1}$ .

$Mn_2SiO_4$ , and  $Co_2SiO_4$  are listed at integral temperatures in Tables 5, 6, and 7 up to 380 K.

At 298.15 K the entropy changes,  $S_{298}^{\circ} - S_0^{\circ}$ , for  $Mg_2SiO_4$ ,  $Mn_2SiO_4$ , and  $Co_2SiO_4$   $94.11 \pm 0.10$ ,  $155.9 \pm 0.4$ , and  $142.6 \pm 0.2 \text{ J/(mol}\cdot\text{K)}$  respectively. The zero point entropy,  $S_0^{\circ}$ , is presumably zero for each of these three olivines. Accordingly, the  $S_T^{\circ} - S_0^{\circ}$  values are equal to  $S_T^{\circ}$  and are the correct values for use in thermodynamic calculations.

#### $Mg_2SiO_4$

Kelley (1943) measured the heat capacity of  $Mg_2SiO_4$  prepared from "a mixture of oxides containing an 0.82% excess of magnesium oxide over the theoretical 2:1 molar ratio was rotated in the chamber of a porcelain ball mill for nine hours to assure intimate mixing. The mixture was moistened, tamped into a nickel cartridge, dried at  $100^{\circ}$ , and finally heated in a tube furnace at  $1150 \pm 20^{\circ}$  for four days under a vacuum of  $10^{-4} \text{ mm}$ . After this treatment, the product contained 3.6% uncombined magnesium oxide. It was reground and similarly heated for five additional days at  $1180 \pm 10^{\circ}$ . Analy-

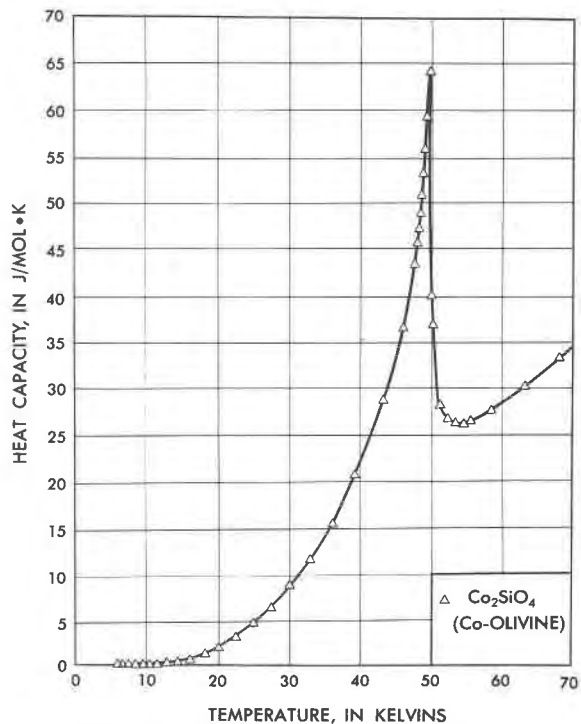


Fig. 3. Molar heat capacity of  $Co_2SiO_4$  in the region of the paramagnetic-antiferromagnetic transition,  $T_N = 49.76 \pm 0.02 \text{ K}$ .

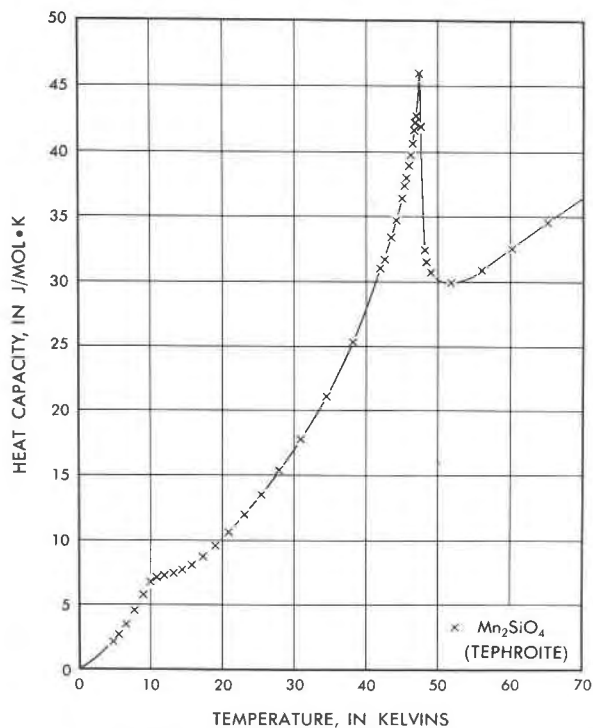


Fig. 4. Molar heat capacity of  $Mn_2SiO_4$  in the region of the low temperature spin ordering transition,  $47.38 \pm 0.05K$ .

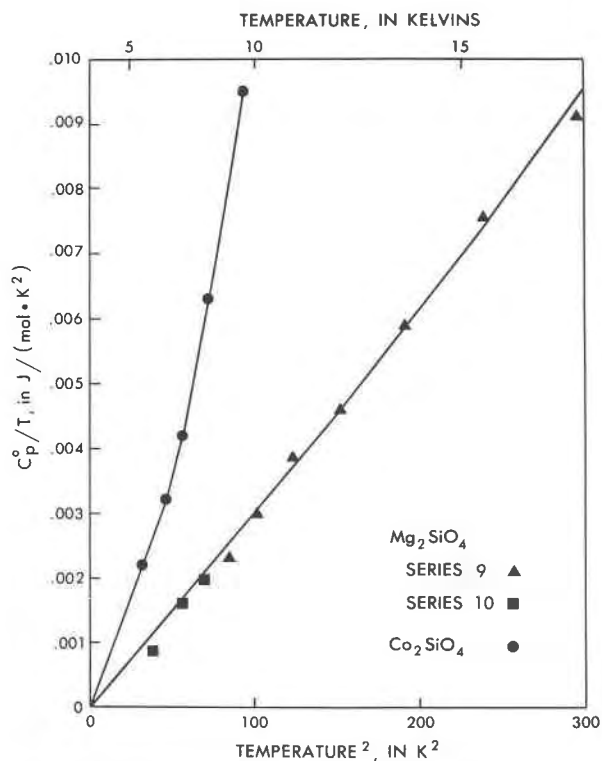


Fig. 5.  $C_p/T$  versus  $T^2$  extrapolation of heat capacity data on  $Mg_2SiO_4$  and  $Co_2SiO_4$  to 0 K.

Table 5. Molar thermodynamic properties of  $Mg_2SiO_4$  (forsterite). Formula weight =  $140.694 \text{ g mol}^{-1}$ .

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY	GIBBS ENERGY
T	$C_p^\circ$	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	0.0032	0.0010	0.0007	0.0003
10	0.0284	0.0088	0.0066	0.0022
15	0.106	0.0327	0.0249	0.0078
20	0.275	0.0834	0.0637	0.0197
25	0.570	0.1736	0.1329	0.0407
30	1.059	0.3169	0.2429	0.0740
35	1.800	0.533	0.410	0.123
40	2.843	0.839	0.646	0.193
45	4.171	1.247	0.961	0.286
50	5.787	1.768	1.361	0.407
60	9.804	3.163	2.419	0.744
70	14.69	5.032	3.814	1.217
80	20.20	7.347	5.513	1.835
90	26.12	10.07	7.471	2.595
100	32.26	13.13	9.642	3.492
110	38.44	16.50	11.98	4.520
120	44.55	20.11	14.44	5.667
130	50.51	23.91	16.99	6.923
140	56.27	27.86	19.59	8.276
150	61.81	31.94	22.22	9.717
160	67.12	36.10	24.86	11.24
170	72.19	40.32	27.50	12.82
180	77.02	44.58	30.12	14.47
190	81.60	48.87	32.71	16.17
200	85.95	53.17	35.26	17.91
210	90.07	57.46	37.77	19.69
220	93.98	61.74	40.24	21.50
230	97.70	66.00	42.66	23.35
240	101.3	70.24	45.03	25.21
250	104.6	74.44	47.34	27.10
260	107.8	78.61	49.61	29.00
270	110.9	82.73	51.82	30.91
280	113.7	86.82	53.98	32.84
290	116.4	90.85	56.09	34.77
300	119.1	94.85	58.14	36.70
310	121.6	98.79	60.15	38.64
320	124.0	102.7	62.11	40.58
330	126.2	106.5	64.01	42.52
340	128.3	110.3	65.87	44.46
350	130.2	114.1	67.68	46.40
360	132.1	117.8	69.45	48.33
370	134.1	121.4	71.17	50.26
380	135.8	125.0	72.85	52.18
273.15	111.0	84.02	52.51	31.52
298.15	118.6	94.11	57.77	36.34

sis now gave 98.6% magnesium orthosilicate, 0.8% uncombined magnesium oxide, no free silica, and no magnesium metasilicate". His  $C_p^\circ$  results (53.2 to 295.0 K) differ from our measurements by a maximum of 0.5 percent over the common temperature range. Our value for  $S_{298}^\circ$ ,  $94.11 \pm .10 \text{ J}/(\text{mol}\cdot\text{K})$  is 1.1 percent less than that obtained by Kelley (1943). Almost all of this difference arises from the *empirical* extrapolation of his data from 50 to 0 K. Over that part of the temperature range for which he actually measured  $C_p^\circ$  his value for  $S_{298}^\circ - S_{50}^\circ$  and ours agree to 0.3 percent.

We have also combined our heat capacity results for the range 300–380 K with the heat content data of Orr (1953) between 398.1 and 1807.6 K to generate values for the molar heat capacity at higher

Table 6. Molar thermodynamic properties of  $Mn_2SiO_4$  (tephroite). Formula weight = 201.960 g mol<sup>-1</sup>.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	$C_p^*$	$(S_T^* - S_0^*)$	$(H_T^* - H_0^*)/T$	$-(G_T^* - H_0^*)/T$
KELVIN		J/(mol·K)		
5	2.211	1.267	0.808	0.459
10	6.893	4.263	2.712	1.551
15	7.760	7.217	4.244	2.973
20	10.08	9.733	5.384	4.349
25	13.21	12.31	6.627	5.682
30	17.05	15.04	8.030	7.011
35	21.76	18.01	9.643	8.367
40	27.74	21.29	11.51	9.774
45	36.08	24.99	13.74	11.25
50	29.91	28.85	16.02	12.83
55	30.71	31.71	17.29	14.42
60	32.49	34.46	18.48	15.98
70	37.29	39.80	20.80	19.00
80	43.29	45.17	23.23	21.94
90	49.42	50.62	25.80	24.82
100	55.41	56.14	28.47	27.68
110	61.23	61.70	31.18	30.52
120	66.80	67.27	33.92	33.35
130	72.08	72.82	36.65	36.17
140	77.07	78.35	39.36	38.98
150	81.81	83.83	42.04	41.79
160	86.30	89.25	44.66	44.59
170	90.56	94.61	47.24	47.37
180	94.57	99.91	49.76	50.15
190	98.36	105.12	52.22	52.90
200	101.9	110.3	54.62	55.64
210	105.3	115.3	56.95	58.36
220	108.5	120.3	59.22	61.07
230	111.6	125.2	61.43	63.75
240	114.5	130.0	63.58	66.41
250	117.2	134.7	65.67	69.05
260	119.8	139.4	67.71	71.66
270	122.3	143.9	69.68	74.25
280	124.7	148.4	71.61	76.82
290	127.0	152.8	73.48	79.37
300	129.1	157.2	75.30	81.89
310	131.2	161.5	77.07	84.39
320	133.1	165.7	78.79	86.86
330	135.1	169.8	80.46	89.31
340	136.9	173.8	82.10	91.74
350	138.6	177.8	83.69	94.14
360	140.2	181.8	85.24	96.52
370	141.8	185.6	86.74	98.88
380	143.0	189.4	88.21	101.21
273.15	123.1	145.4	70.30	75.07
298.15	128.7	156.4	74.96	81.43

Table 7. Molar thermodynamic properties of  $Co_2SiO_4$ . Formula weight = 209.950 g mol<sup>-1</sup>.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	$C_p^*$	$(S_T^* - S_0^*)$	$(H_T^* - H_0^*)/T$	$-(G_T^* - H_0^*)/T$
KELVIN		J/(mol·K)		
5	0.0050	0.0014	0.0010	0.0004
10	0.101	0.023	0.0186	0.0045
15	0.574	0.130	0.106	0.024
20	1.975	0.458	0.372	0.086
25	4.607	1.159	0.935	0.224
30	8.555	2.326	1.856	0.470
35	14.13	4.039	3.188	0.851
40	21.71	6.393	5.003	1.390
45	33.18	9.553	7.440	2.113
50	38.50	14.22	11.15	3.069
55	26.41	16.80	12.60	4.20
60	28.70	19.19	13.84	5.355
70	34.75	24.05	16.38	7.677
80	41.64	29.14	19.10	10.04
90	48.59	34.45	21.99	12.45
100	55.27	39.92	24.99	14.93
110	61.58	45.48	28.03	17.45
120	67.53	51.10	31.08	20.02
130	73.14	56.73	34.10	22.63
140	78.44	62.34	37.08	25.26
150	83.46	67.93	40.01	27.92
160	88.19	73.47	42.87	30.60
170	92.65	78.95	45.67	33.28
180	96.86	84.36	48.40	35.97
190	100.8	89.71	51.05	38.66
200	104.6	94.98	53.64	41.34
210	108.1	100.2	56.15	44.02
220	111.5	105.3	58.59	46.69
230	114.8	110.3	60.96	49.34
240	117.9	115.3	63.27	51.99
250	120.9	120.1	65.52	54.62
260	123.8	124.9	67.71	57.23
270	126.5	129.7	69.83	59.82
280	129.1	134.3	71.91	62.40
290	131.6	138.9	73.92	64.96
300	133.9	143.4	75.88	67.50
310	136.1	147.8	77.79	70.02
320	138.2	152.2	79.64	72.52
330	140.2	156.4	81.45	75.00
340	142.2	160.7	83.20	77.45
350	144.1	164.8	84.92	79.89
360	146.0	168.9	86.59	82.31
370	147.7	172.9	88.22	84.70
380	149.3	176.9	89.80	87.07
273.15	127.4	131.1	70.49	60.64
298.15	133.4	142.6	75.52	67.03

temperatures;

$$C_p = 87.36 + 0.08717T - 3.699 \times 10^{-6}T^2 + 843.6T^{-0.5} - 2.237 \times 10^{-5}T^2$$

(298–1800K). This equation fitted the 23 data points with an average deviation of 0.2 percent and joins the low temperature  $C_p^0$  curve smoothly.

The enthalpy change for the reaction



has been measured by Torgeson and Sahama (1948), and King *et al.* (1967) by HF(aq) solution calorimetry. These authors' results were corrected by Hemingway and Robie (1977) for  $SiO_2$  particle size effect. Navrotsky (1971) obtained  $-62.8 \pm 4.2$  kJ for  $\Delta H_{965}^0$  (1) by molten salt calorimetry. Her

value is however based on an *estimated* value for  $\Delta H_{soln}$  of MgO in the molten  $2PbO \cdot B_2O_3$  used to dissolve  $Mg_2SiO_4$  and  $SiO_2$ . This *estimated* value for  $\Delta H_{soln}$  of MgO in the  $2PbO \cdot B_2O_3$  melt has the opposite sign from that *measured* at a later time by Navrotsky and Coons (1976) at a slightly different temperature and we therefore did not include this result in our analysis. Charlou *et al.* (1975) obtained  $-62.6 \pm 1.1$  kJ at 970 K and Kiseleva *et al.* (1979) obtained  $-58.2 \pm 1.4$  kJ for  $\Delta H_{973}^0$  for this reaction both by molten salt solution calorimetry. Kiseleva *et al.* (1979) value corrected to 298 K using the heat capacity data of Robie *et al.* (1979) yields  $\Delta H_{298}^0 = -56.5$  kJ, and is in excellent agreement with that adopted by Robie *et al.* (1979, p. 364),  $\Delta H_{298}^0 = -56.7 \pm 0.7$  kJ/mol which we believe is the best

Table 8. Thermodynamic properties of  $Mg_2SiO_4$  at high temperature and  $\Delta H^\circ$  and  $\Delta G^\circ$  for the reaction  $2MgO + SiO_2 = Mg_2SiO_4$ .

TEMP.	$(H_T - H_{298})/T$	$S_T^\circ$	$-(G_T - H_{298})/T$	$C_p^\circ$	ENTHALPY	GIBBS FREE ENERGY
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol
298.15	0.00	94.11 ± .10	94.11 ± .10	118.60	-56.69 ± .69	-56.32 ± .71
400	32.92	131.97	99.05	137.71	-56.73	-56.20
500	55.01	163.92	108.91	148.28	-56.84	-56.05
600	71.21	191.65	120.44	155.77	-57.12	-55.87
700	83.73	216.12	132.39	161.75	-57.53	-55.62
800	93.81	238.06	144.25	166.83	-58.06	-55.33
900	102.17	257.97	155.80	171.25	-59.00	-54.91
1000	109.28	276.22	166.94	175.14	-58.71	-54.46
1100	115.43	293.08	177.65	178.56	-58.28	-54.07
1200	120.81	308.74	187.93	181.54	-57.74	-53.71
1300	125.59	323.38	197.79	184.09	-57.10	-53.41
1400	129.84	337.10	207.26	186.22	-56.39	-53.13
1500	133.66	350.01	216.35	187.93	-55.52	-52.93
1600	137.10	362.18	225.08	189.22	-54.84	-52.78
1700	140.19	373.68	233.49	190.09	-54.05	-52.66
1800	142.98	384.56	241.59	190.54	-53.29	-52.62

value. Combining this value with the enthalpies of formation of periclase and quartz from Robie *et al.*, we obtain  $\Delta H_{f,298}^\circ = -2170.4 \pm 1.4$  kJ/mol. Using the entropies of the elements adopted by Robie *et al.* and the entropy of forsterite obtained in the present work we get  $\Delta G_{f,298}^\circ = -2051.0 \pm 1.4$  kJ/mol.

The heat capacity equation for forsterite was combined with the value of  $\Delta H_{f,298}^\circ$  adopted above and the high temperature thermodynamic functions for periclase and quartz tabulated by Robie *et al.* (1979) to obtain the values of  $\Delta H_T^\circ$  and  $\Delta G_T^\circ$  listed in Table 8. Our values for  $\Delta G_T^\circ$  differ significantly from those obtained by the e.m.f. measurements of Rog *et al.* (1974) between 1373 and 1573 K.

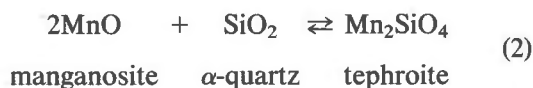
### $Mn_2SiO_4$

King and Weller's measurements on  $Mn_2SiO_4$  between 52.3 and 296.1 K (Mah, 1960) were made on "crystalline manganese orthosilicate (tephroite)" with no further description of the preparation of the material. Their measured values are systematically larger than ours, being about 2 per cent greater at 50 K and decreasing to +0.7 per cent at 300 K. Their entropy value at 298 K includes an empirical extrapolation below 51.0 K of 24.9 J/(mol·K) and was apparently made without any knowledge of the two low-temperature magnetic transitions. In the same way as described for  $Mg_2SiO_4$  we combined our low temperature  $C_p^\circ$  data with the heat content measurements of Christensen (Mah, 1960) to generate

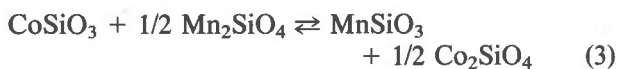
$$C_p^\circ = 261.28 - 1.378 \times 10^{-2} T - 2217.7 T^{-0.5} \quad (298-1600 \text{ K})$$

for  $Mn_2SiO_4$ .

Jeffes *et al.* (1954) obtained  $\Delta H_{298}^\circ = -49.2 \pm 2.9$  kJ for the reaction



by HF(aq) solution calorimetry (at 25°C). Hemingway and Robie (1977) adjusted this result to  $-47.1 \pm 3.0$  kJ to account for the very fine particle size of the quartz used in the  $\Delta H_{sol}$  measurements. Navrotsky and Coons (1976) obtained  $\Delta H_{298}^\circ = -48.5 \pm 1.4$  kJ for this reaction using molten  $2PbO \cdot B_2O_3$  as the solvent. Schwerdtfeger and Muan (1966) give  $-43.5 \pm 1.7$  kJ for the Gibbs free energy change,  $\Delta G_r^\circ$ , for this reaction at 1423 K based on measurements of the equilibrium gas ratios of CO/CO<sub>2</sub> coexisting with phases in the "FeO"-MnO-SiO<sub>2</sub> system. Biggers and Muan (1967) obtained  $\Delta G_{r,1523}^\circ = -42.3 \pm 3.4$  kJ from equilibrium measurements of the exchange reaction



combined with the  $\Delta G^\circ$  values for  $Co_2SiO_4$  from Lebedev *et al.* (1962) and Aukrust and Muan (1963).

Using  $\Delta G_r^\circ$  from Schwerdtfeger and Muan, and Biggers and Muan, and our heat capacity (and entropy) data together with those for MnO and SiO<sub>2</sub> tabulated by Robie *et al.* (1979) we can also obtain a value for  $\Delta H_{298}^\circ$  for reaction (2) as follows: from the heat capacity data, we obtain  $\Delta S_{r,1423}^\circ$  and from the relation

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

we get  $\Delta H_{r,1423}^\circ$  and using Kirchoff's relation calculate  $\Delta H_{r,298}^\circ = -53.7 \pm 2.1$  kJ from Schwerdtfeger and Muan and  $-53.5 \pm 4.4$  kJ, from Biggers and Muan respectively. Schreiber (1963) studied the reaction



between 738 and 813 K. From his equation for  $\log f_{CO_2}$  as a function of temperature and our entropy data, and using unpublished measurements of Robie and Hemingway on the entropy of  $MnCO_3$ , we get  $\Delta G_{700}^\circ = -44.2$  kJ/mol for the formation of  $Mn_2SiO_4$  from the oxides, and  $-49.3$  kJ/mol for  $\Delta H_{700}^\circ$  (2).

The agreement between the 5 independent values is only fair and we therefore simply adopted a



rounded average for  $\Delta H_{f,298}^\circ$  (2) of  $-50.8 \pm 2.5$  kJ/mol. We combined this value with ancillary data from Robie *et al.* (1979) to obtain  $-1732.0 \pm 2.9$  and  $-1631.5 \pm 3.0$  kJ/mol for  $\Delta H_{f,298}^\circ$  and  $\Delta G_{f,298}^\circ$  respectively. In Table 9 we list the high temperature thermodynamic properties for tephroite together with  $\Delta H_T^\circ$  and  $\Delta G_T^\circ$  for reaction (2).

### $Co_2SiO_4$

There are apparently no high temperature heat capacity data for  $Co_2SiO_4$ . At 298.15 K  $\Delta S^\circ$  is  $-4.8 \pm 0.4$  J/K for reaction (5) based on our entropy for  $Co_2SiO_4$  and those tabulated by Robie and others (1979) for CoO and  $SiO_2$ . In order to use the high temperature equilibrium data we have estimated the heat capacity of  $Co_2SiO_4$  between 400 and 1500 K by using the sum of the heat capacities of 2 moles of CoO and 1 of  $SiO_2$ , joining these estimates smoothly with our measured values for  $Co_2SiO_4$  between 300 and 380 K, making proper allowance; that is, by smoothing thru the temperature region of anomalous heat capacities caused by the  $\alpha$ - $\beta$  transition in quartz. Our estimated heat capacities for  $Co_2SiO_4$  are represented by the equation

$$C_p^\circ = 343.9 - 0.1006T + 3.814 \times 10^{-5}T^2 - 3175T^{-0.5} \quad (289-1500 \text{ K})$$

This equation was used together with our measured entropy at 298.15 K to calculate  $S_T^\circ$  and  $H_T^\circ - H_{298}^\circ$  for use in a third-law treatment of the high temperature equilibrium studies on  $Co_2SiO_4$ .

Navrotsky (1971) and Navrotsky *et al.* (1979) obtained  $\Delta H_{965}^\circ = -21.6 \pm 2.1$ , and  $\Delta_{986}^\circ = -23.0 \pm 0.8$  kJ respectively, for the reaction



by solution calorimetry using  $2PbO \cdot B_2O_3$  as the solvent. The Gibbs energy change for this reaction has been determined by Lebedev *et al.* (1963) between 1073 and 1423 K, and by Aukrust and Muan (1963) (1273–1573 K) by CO reduction equilibria, and by Kozłowska-Rog and Rog (1979) by solid state emf studies.

We have used the experimental data of Lebedev *et al.* (1962) and of Aukrust and Muan (1963) for the equilibrium



over the temperature range 1083 to 1573 K. To the experimental  $\Delta G_T^\circ$  data of Lebedev *et al.* for (5) we added  $\Delta G_T^\circ$  for the reaction

Table 9. Thermodynamic properties of  $Mn_2SiO_4$  at higher temperatures and  $\Delta H^\circ$  and  $\Delta G^\circ$  for the reaction  $2MnO + SiO_2 = Mn_2SiO_4$ .

TEMP. K	$(H_T^\circ - H_{298}^\circ)/T$ J/mol·K	$S_T^\circ$ J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	$C_p$ J/mol·K	ENTHALPY kJ/mol	GIBBS FREE ENERGY kJ/mol
298.15	0.00	155.90 ±0.40	155.90 ±0.40	128.50 ±0.15	-50.84 ±2.50	-49.36 ±2.60
400	35.00	196.17	161.17	144.84	-51.13	-48.79
500	58.06	229.67	171.61	155.17	-51.32	-48.19
600	74.88	258.64	183.76	162.43	-51.54	-47.54
700	87.79	284.10	196.31	167.77	-51.90	-46.86
800	98.05	306.78	208.73	171.80	-52.47	-46.09
900	106.42	327.20	220.78	174.91	-53.55	-45.24
1000	113.40	345.76	232.36	177.33	-53.56	-44.30
1100	119.30	362.76	243.46	179.21	-53.63	-43.37
1200	124.36	378.41	254.05	180.68	-53.78	-42.42
1300	128.74	392.92	264.18	181.81	-54.05	-41.47
1400	132.56	406.43	273.87	182.67	-54.46	-40.49
1500	135.92	419.06	283.14	183.30	-55.00	-39.46
1600	138.90	430.90	292.00	183.74	-55.72	-38.41
1620	139.45	435.21	295.75	183.81	-55.74	-41.09



using data from Robie *et al.* (1979) for  $SiO_2$  and the JANAF Thermochemical Tables for CoO to obtain  $\Delta G_T^\circ$  (1083–1573 K) for reaction (6). We did not use the equation given by Lebedev *et al.* for reaction (5) because in deriving it from their experimental data, they had used values for  $\Delta G_{f,T}^\circ$  for CO taken from Richardson and Jeffes (1949) which are incorrect. Aukrust and Muan (1963) obtained their  $\Delta G_T^\circ$  values for (5) by combining their equilibrium constants for (6) with their own measurements for (7).  $\Delta G_T^\circ$  for reaction (5) from the CO reduction equilibrium studies are in reasonable agreement but are  $\approx 3$  kJ more negative than the  $\Delta G^\circ$  obtained from the emf measurements. A third-law treatment of these data leads to  $\Delta H_{298}^\circ$  for reaction (5) of  $-23.0 \pm 1.5$  kJ. Combining our values with  $\Delta H_{f,298}^\circ$  for CoO and  $SiO_2$  from JANAF (1971) or Robie *et al.* (1979), we obtain  $\Delta G_{f,298}^\circ = -1305.8 \pm 3.0$  kJ/mol and  $\Delta H_{f,298}^\circ = -1411.6 \pm 2.9$  kJ/mol for  $Co_2SiO_4$  (from the elements).

At 975 K, the mean temperature of the molten salt calorimetric determination of  $\Delta H^\circ$  for reaction (5), our treatment yields  $-27.9$  kJ. This is approximately 5.6 kJ more negative than the value given by Navrotsky *et al.* (1979).

### Magnetic entropies and heat capacities of $Mn_2SiO_4$ and $Co_2SiO_4$

In order to separate the magnetic contributions to the heat capacity from those arising from the lattice vibrations we have adopted the corresponding

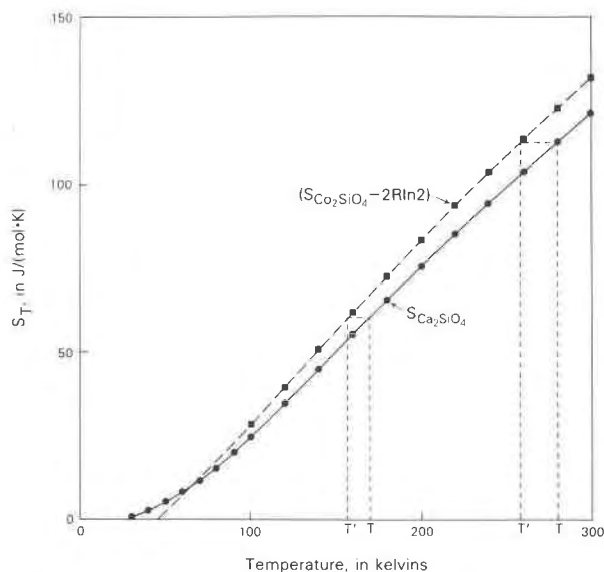


Fig. 6. Plot of the entropy of  $\gamma\text{-Ca}_2\text{SiO}_4$  and the quantity  $S_{\text{Co}_2\text{SiO}_4} - 2R\ln 2$ .

states model suggested by Stout and Catalano (1955). We used both our  $C_p^\circ$  data for  $Mg_2SiO_4$  and those of King (1957) for  $\gamma\text{-Ca}_2SiO_4$  with the corresponding states model to estimate the lattice entropies of  $Mn_2SiO_4$  and  $Co_2SiO_4$ .<sup>1</sup>

We proceeded as follows: first, from a large scale plot of our smoothed values for the molar heat capacity of  $Mg_2SiO_4$  and those of King (1957) for  $\gamma\text{-Ca}_2SiO_4$ , which cover only the range 52 to 295 K, we calculated the ratio  $T/T'$  where  $T'$  is the temperature at which  $C_p^\circ$  of  $\gamma\text{-Ca}_2SiO_4$  is the same as  $C_p^\circ$  for  $Mg_2SiO_4$  at the temperature  $T$ . The ratio  $T/T'$  was then plotted as a function of temperature and extrapolated to zero kelvin. From the extrapolated values of  $T/T'$  and our measured value of  $C_p^\circ(T)$  of  $Mg_2SiO_4$  we generated values of  $C_p^\circ$  for  $\gamma\text{-Ca}_2SiO_4$  for temperatures between 5 and 52 K. These estimated values for  $C_p^\circ$  of  $\gamma\text{-Ca}_2SiO_4$  were combined with King's measured values above 52 K to calculate  $S_T^\circ$  for  $\gamma\text{-Ca}_2SiO_4$  at 5 K intervals. Next we plotted  $S_T^\circ$  for  $\gamma\text{-Ca}_2SiO_4$  and the quantity  $(S_T^{\circ\text{meas.}} - 2R\ln 6)$  for  $Mn_2SiO_4$  where  $2R\ln 6$  is the limiting value for the magnetic entropy at high temperature, and derived the ratio  $T/T'$  where again  $T'$  is the

<sup>1</sup>Although neither  $Mg_2SiO_4$  or  $\gamma\text{-Ca}_2SiO_4$  are ideal models for calculating the lattice heat capacity or entropies of the transition metal olivines, we use them because  $Zn_2SiO_4$ , which would have been a more satisfactory model, does not crystallize in the olivine structure—even up to 150 kilobars (15 MPa) pressure, (Syono *et al.* 1971).

temperature at which the quantity  $(S_T^\circ - 2R\ln 6)$  for  $Mn_2SiO_4$  has the same value as  $S^\circ(\text{Ca}_2SiO_4)$  at the temperature  $T$ , see Figure 6. This ratio was linearly extrapolated to 0 K and used to estimate the lattice entropies for  $Mn_2SiO_4$ . This estimated lattice entropy was then subtracted from our smoothed values for the total entropy of  $Mn_2SiO_4$ , listed in Table 5, to obtain the entropy associated with the ordering of the magnetic moments of the  $Mn^{2+}$  ions. The resultant magnetic entropy is shown in Figure 7. Our measurements for  $Co_2SiO_4$  were treated in a similar fashion. For  $Co^{2+}$  the spin quantum number  $S$  is 3/2. However, at low temperature  $Co^{2+}$  frequently behaves as though  $S$  were 1/2, that is the effective spin  $S' = 1/2$  (*e.g.*, Carlin and van Duynveldt, 1977, p. 64–71) and accordingly for our corresponding states estimation of the lattice entropy we used the quantity  $(S_T^\circ - 2R\ln 2)$  for  $Co_2SiO_4$ . We therefore expect the magnetic entropy of  $Co_2SiO_4$  to approach  $2R\ln 2$  for  $T \gg T_N$  and this is in fact what we observed.

From Figure 7 we see that for  $Mn_2SiO_4$  the magnetic entropy is only about 75 percent of  $2R\ln 6$  (29.79 J/mol·K) at the Néel temperature, and that of  $Co_2SiO_4$  is only about 71 percent of  $2R\ln 2$  (11.53 J/

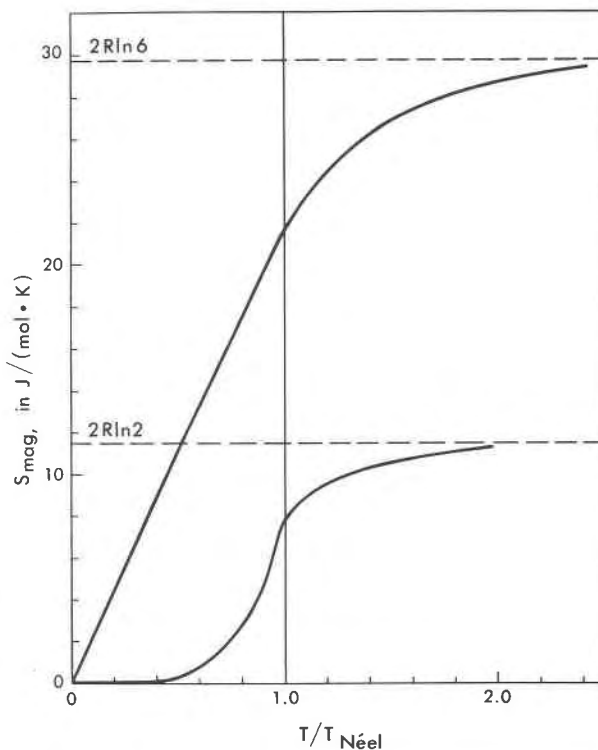


Fig. 7. Magnetic entropies of  $Co_2SiO_4$  and  $Mn_2SiO_4$ .

mol·K) at  $T_N$ . This indicates that appreciable short range order is retained by the magnetic spin systems at temperatures well above  $T_N$  and in fact the total expected magnetic entropies are not fully excited until temperatures of the order of twice the Néel temperature have been reached.

The lattice heat capacities of  $Mn_2SiO_4$  and  $Co_2SiO_4$  were derived from our *estimated* lattice entropies utilizing the thermodynamic relation

$$C_{lat} = T(dS_{lat}/dT)$$

Values for  $C_{lat}$  so obtained were subtracted from our *measured* total molar heat capacities (Figs. 4 and 5) to obtain the magnetic heat capacities of  $Mn_2SiO_4$  and  $Co_2SiO_4$  listed in Tables 10 and 11.

#### The Debye temperature of $Mg_2SiO_4$

The Debye temperature,  $\theta_D$  is the most useful *single* parameter for characterizing the thermal properties of a solid. The Debye temperature may be calculated from low temperature heat capacity measurements from equation (8)

$$\theta_D^C = [(12/5)q\pi^4RT^3/C_V]^{1/3} \quad (8)$$

where  $q$  is the number of atoms in the "molecule" and  $R$  is the gas constant (8.3143 J/(mol·K)). This relation is strictly rigorous only for temperatures of the order of  $T < \theta_D/50$ , Blackman (1955). From our

Table 10. Magnetic heat capacity of  $Mn_2SiO_4$  (tephroite) in the neighborhood of the Néel temperature, 47.38 K.

Temp Kelvins	$C_p$ (total) J/(mol K)	$C_{lat}$ . J/(mol K)	$C_{mag}$ . J/(mol K)
34.25	20.94	5.68	15.26
38.10	25.26	7.67	17.58
42.23	30.49	9.94	20.55
42.72	31.62	10.27	21.35
43.61	33.20	10.81	22.39
44.39	34.71	11.29	23.42
45.09	36.23	11.74	24.49
45.57	36.88	12.04	24.84
45.85	38.19	12.15	26.04
46.14	39.35	12.40	26.95
46.42	39.92	12.58	27.34
46.64	41.00	12.73	28.27
46.81	41.60	12.84	28.76
47.00	42.75	12.96	29.79
47.18	43.56	13.08	30.48
47.68	41.92	13.41	28.51
48.04	30.71	13.65	17.06
48.42	29.58	13.91	15.67
48.81	29.02	14.17	14.85
51.72	29.83	16.14	13.69
52.99	30.99	17.04	13.95

Table 11. Magnetic heat capacity of  $Co_2SiO_4$  (cobalt olivine) in the neighborhood of the Néel temperature, 49.76 K.

Temp Kelvins	$C_p$ (total) J/(mol K)	$C_{lat}$ . J/(mol K)	$C_{mag}$ . J/(mol K)
39.41	20.67	8.85	11.82
43.28	28.55	11.38	17.17
46.05	36.48	13.22	23.26
47.69	43.40	14.31	29.09
48.08	45.71	14.57	31.14
48.32	47.21	14.73	32.48
48.54	48.92	14.88	34.04
48.76	50.84	15.04	35.80
48.97	53.15	15.18	37.97
49.17	55.80	15.33	40.47
49.37	59.31	15.47	43.84
49.55	64.05	15.60	48.45
49.95	39.47	15.88	23.59
50.12	32.77	16.01	16.76
51.02	27.67	16.67	11.00
52.10	26.62	17.46	9.16
53.17	26.21	18.26	7.95
54.23	26.30	19.10	7.20
55.25	26.51	19.78	6.73

heat capacity results for  $T < 15$  K, Table 1, we obtain  $\theta_D^C = 768 \pm 15$  K.

The Debye temperature is also related to the mean velocity of sound in a solid by relation (9)

$$\theta_D^E = (h/k)[3qN\rho/4\pi M]^{1/3}v_m \quad (9)$$

where  $h$  is Planck's constant ( $6.62618 \times 10^{-34}$  J·sec),  $k$  is Boltzman's constant ( $1.38066 \times 10^{-23}$  J·K<sup>-1</sup>),  $q$  is the number of atoms in the "molecule",  $N$  is Avogadro's number ( $6.02209 \times 10^{23}$  mol<sup>-1</sup>),  $\rho$  is the density in g·cm<sup>-3</sup>, and  $M$  the formula weight in grams. Robie and Edwards (1966) have shown how the mean sound velocity,  $v_m$ , may be calculated for a crystal of any symmetry from the single crystal elastic constants and the density by means of numerical integration with a computer.

We have calculated the Debye temperature of synthetic forsterite from the room temperature elastic stiffness constants ( $c_{ij}$ ) of Graham and Barsch (1969), and of Sumino *et al.* (1977) using a modified (FORTRAN.IV) version of the computer program mentioned by Robie and Edwards (1966). These calculations yield  $v_m = 5.553$  and  $5.532$  km/sec from the data of Graham and Barsch and from Sumino *et al.* respectively. The corresponding  $\theta_D^E(298)$  are 757.9 and 755.9 K. Sumino *et al.* (1977) also measured the elastic constants at 83 K from which we obtained  $v_m = 5.604$  km/sec and  $\theta_D^E(83) = 766.6$  K. From results of Sumino *et al.* we estimate  $\theta_D^E(0) =$

768.6 K which is in excellent agreement with our calorimetric value.

At the lowest temperatures of our measurements, the heat capacity of  $Mn_2SiO_4$  and  $Co_2SiO_4$  are composed of a lattice (Debye) term *plus* a contribution arising from the spin waves (magnons) (see for example, Gopal, 1966). Both of these terms vary as  $T^3$  and accordingly we cannot evaluate their Debye temperatures ( $\theta_D^E$ ) from our measurements. One may however make a first order estimate of the coefficient of the spin wave term as follows: from the room temperature elastic constant values of Sumino (1979) for  $Mn_2SiO_4$  and  $Co_2SiO_4$  one calculates  $\theta_D^E$  of 533 and 548 K respectively. Assuming these (elastic) Debye temperatures to be independent of temperature, the lattice heat capacity may be calculated from (10)

$$C_V = [12/5 \pi^4 q R T^3] / \theta_D^3 \quad (10)$$

for  $T < \theta_D/50$ . This calculated lattice heat capacity is then subtracted from the measured (total) heat capacity to obtain that arising from the spin waves. At 10 K for  $Co_2SiO_4$  the spin wave heat capacity is approximately 18 percent of the measured molar  $C_p^\circ$ .

### Acknowledgments

This work was in part supported by the U.S. Department of Energy through the Los Alamos Scientific Laboratory, contract X69-9915F-3. We thank our U.S. Geological Survey colleagues, H.T. Haselton, Jr., and Susan Werner Kieffer for their many useful suggestions for improving the manuscript.

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*Manuscript received, July 20, 1981;  
accepted for publication, January 20, 1982.*