American Mineralogist, Volume 67, pages 470–482, 1982

Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 between 5 and 380 K

RICHARD A. ROBIE, BRUCE S. HEMINGWAY

U.S. Geological Survey
Reston, Virginia 22092

AND HUMIHIKO TAKEI

Research Institute for Iron, Steel and other Metals
Tohoku University, Sendai, Japan

Abstract

The heat capacities of synthetic single crystals of Mg_2SiO_4 (forsterite), Mn_2SiO_4 (tephroite), and Co_2SiO_4 (cobalt olivine), were measured between 5 and 380 K using an adiabatically shielded calorimeter. Mg_2SiO_4 is diamagnetic, and its heat capacity follows a normal sigmoidal curve at low temperatures. Co_2SiO_4 shows a single sharp λ-type transition at 49.85±0.02 K associated with the antiferromagnetic ordering of the magnetic moments of the Co^{2+} ions into a collinear spin arrangement below 49.8 K. In contrast to Co_2SiO_4, Mn_2SiO_4 has two transitions in C_p°, a sharp λ-type transition at 47.38±0.05 K and a smaller "shoulder" in C_p° centered near 12 K. The upper transition corresponds to the paramagnetic (disordered) to collinear antiferromagnetic ordering of the 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±2 K and 50±5 K for Co_2SiO_4 and Mn_2SiO_4 respectively.

The thermal Debye temperature, θ_D^C, of Mg_2SiO_4 calculated from our C_p° measurements between 6.3 and 13.8 K is 768±15 K and agrees well with the elastic value θ_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±0.10, 155.9±0.4 and 142.6±0.2 J/(mol · K) respectively for Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_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 $M_2(SiO_4)$ 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. γ-Ca_2SiO_4 (calcio-olivine) occurs very rarely in nature and Co_2SiO_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 γ-Ca_2SiO_4 is important in the phase chemistry of Portland cement clinker.

The crystal structure of the olivine form of Mg_2SiO_4 has been refined by Hazen (1976) and that of Co_2SiO_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

0003–004X/82/0506–0470$02.00

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° 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 $H_T^\circ - H_{298}^\circ$ 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 (≈1900°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 (≈1350°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 4×10^{-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^{-1} 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 (ΔT<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 λ-type transition in C_p° 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° 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 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.

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

Temp. K	Heat capacity J/(g·K)	Temp. K	Heat capacity J/(g·K)	Temp. K	Heat capacity 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	
Series 2		177.63	0.5395		
				7.66	0.000018
335.44	0.9053	Series 6		9.14	0.000149
341.31	0.9134			10.10	0.000215
346.97	0.9224	175.31	0.5315	11.11	0.000306
		180.79	0.5499	12.35	0.000401
Series 3		186.41	0.5685	13.82	0.000578
		192.02	0.5862	15.47	0.000830
351.06	0.9259	197.73	0.6039	17.22	0.001004
355.20	0.9324	203.46	0.6211	19.18	0.001698
360.95	0.9407	209.08	0.6375	21.46	0.002463
367.13	0.9494			23.71	0.003402
373.75	0.9575	Series 7		25.85	0.004524
380.31	0.9654				
		207.86	0.6338	Series 10	
Series 4		213.42	0.6495		
		219.11	0.6655	6.23	0.000037
52.87	0.04915	224.92	0.6811	7.56	0.000086
58.53	0.06511	230.62	0.6961	8.44	0.000117
63.54	0.08114	236.40	0.7107		
68.82	0.09976	242.25	0.7249	Series 11	
74.21	0.1203	248.01	0.7389		
79.63	0.1421	253.84	0.7527	26.04	0.004621
85.16	0.1652	259.74	0.7662	28.68	0.006425
90.77	0.1892	265.56	0.7783	31.43	0.008845
96.41	0.2137			34.70	0.01244
101.99	0.2380			38.25	0.01732
107.50	0.2622			41.85	0.02330
112.83	0.2854			45.88	0.03133
118.02	0.3080			50.12	0.04158
123.10	0.3298				
128.25	0.3516				

For Mn_2SiO_4 and Co_2SiO_4 we made replicate measurements in the region of the C_p° 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°/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		Series X	
303.63	129.8	219.57	108.4
309.63	131.1	225.53	110.2
315.36	132.2	231.42	112.0
321.05	133.3	237.32	113.7
326.69	134.4	243.24	115.3
Series II		Series XI	
326.48	134.4	249.12	115.4
332.30	135.7	254.96	116.8
338.57	136.8		
344.78	137.6	Series XI	
350.94	138.7	250.11	117.2
357.16	139.7	256.03	118.8
363.43	140.7	261.97	120.3
369.66	141.7	267.92	121.8
375.84	142.6	273.88	123.3
381.99	143.3	279.85	124.7
		285.75	126.0
Series III		291.69	127.5
51.72	29.83		
52.99	30.99	Series XIII	
60.04	32.60	4.65	1.987
		5.57	2.625
Series IV		6.50	3.402
65.18	34.68	7.50	4.607
70.06	37.31	8.53	5.830
74.97	40.23	9.68	6.800
		10.70	7.159
Series V		11.70	7.186
78.12	42.14	12.89	7.291
83.42	45.40	14.21	7.537
88.67	48.58	15.65	7.926
94.22	51.96	17.21	8.613
		18.91	9.466
Series VI		20.86	10.55
83.70	45.58	22.99	11.89
88.79	48.69	25.24	13.41
93.96	51.82	27.75	15.23
99.60	55.19	30.78	17.74
		34.25	20.94
Series VII		38.10	25.26
100.39	55.66	42.23	30.49
106.06	58.97	46.55	43.58*
111.53	62.08		
117.19	65.24	Series XIV	
122.92	68.37	42.72	31.62
128.52	71.32	43.61	33.20
134.02	74.13	44.30	34.71
139.36	75.75	45.09	36.23
144.73	79.37	45.57	36.88
150.17	81.91	45.85	38.19
155.67	84.38	46.14	39.35
		46.42	39.92
Series VIII		46.64	41.00
161.29	86.84	46.81	41.60
167.17	89.32	47.00	42.75
172.98	91.77	47.18	43.56
178.87	94.17	47.39	46.06
184.83	96.44	47.68	41.92
190.75	98.64	48.04	30.71
		48.42	29.58
Series IX		48.81	29.02
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		Series VII	
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		Series VIII	
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	Series IX	
380.80	149.5	251.20	121.2
		257.18	123.0
Series III		263.04	124.6
50.12	32.77	268.85	126.2
51.02	27.67	274.59	127.7
52.10	26.62	280.25	129.2
53.17	26.21	285.90	130.6
54.23	26.30	291.50	132.0
55.25	26.51	297.06	133.1
58.13	27.65		
62.97	30.27	Series X	
67.90	33.39	7.53	.0236
72.92	36.77	9.57	.0825
77.97	40.27	10.61	.1295
83.05	43.83	11.64	.1902
88.21	47.37	12.89	.2933
		14.38	.4813
Series IV		16.13	.7989
88.63	47.67	18.06	1.302
94.10	51.34	20.07	2.023
99.36	54.81	22.41	3.088
104.60	58.16	24.94	4.566
109.96	61.50	27.45	6.359
115.54	64.89	30.08	8.627
121.25	68.26	32.91	11.58
126.87	71.45	35.95	15.39
		39.41	20.67
Series V		43.28	28.55
132.52	74.57		
138.28	77.64	Series XI	
143.82	80.43	5.76	.0081
149.40	83.16	6.76	.0182
155.02	85.85	7.51	.0288
160.78	88.53	8.46	.0513
166.66	91.16	9.65	.0880
		10.78	.1380
Series VI			
172.37	93.62	Series XII	
177.95	95.98	46.05	36.48
183.61	98.30	47.69	43.40
189.35	100.6	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 ±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 ±5 percent between 5 and 15 K, increasing in accuracy to ±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 ±1.0 percent.

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

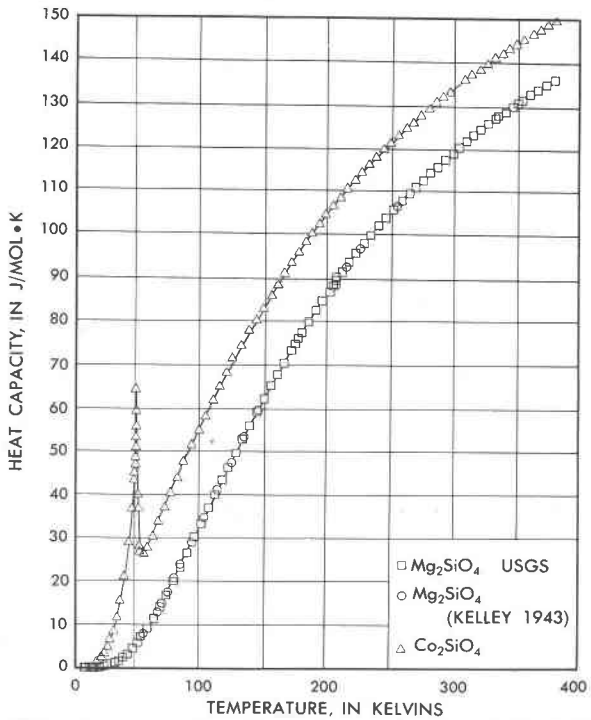

Fig. 1. Experimental molar heat capacity of synthetic single crystal Mg_2SiO_4 (forsterite), formula weight 140.694 g mol^{-1} and synthetic single crystal Co_2SiO_4 formula weight 209.950 g mol^{-1}. Earlier measurements of Kelley (1943) on powdered Mg_2SiO_4 between 53.2 and 295.0 K are shown for comparison.

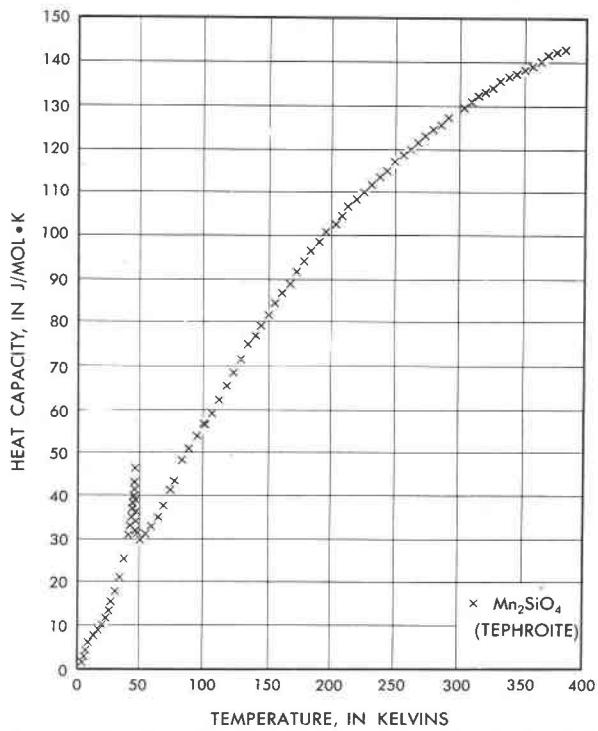

Fig. 2. Experimental molar heat capacities of synthetic single crystal Mn_2SiO_4 (tephroite), formula weight = 201.960 g mol^{-1}.

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, $S^\circ_{298}-S^\circ_0$, for Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 94.11±0.10, 155.9±0.4, and 142.6±0.2 J/(mol·K) respectively. The zero point entropy, S°_0, is presumably zero for each of these three olivines. Accordingly, the $S^\circ_T-S^\circ_0$ values are equal to S°_T 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°, and finally heated in a tube furnace at 1150±20° for four days under a vacuum of 10^{-4} mm. After this treatment, the product contained 3.6% uncombined magnesium oxide. It was reground and similarly heated for five additional days at 1180±10°. Analy-

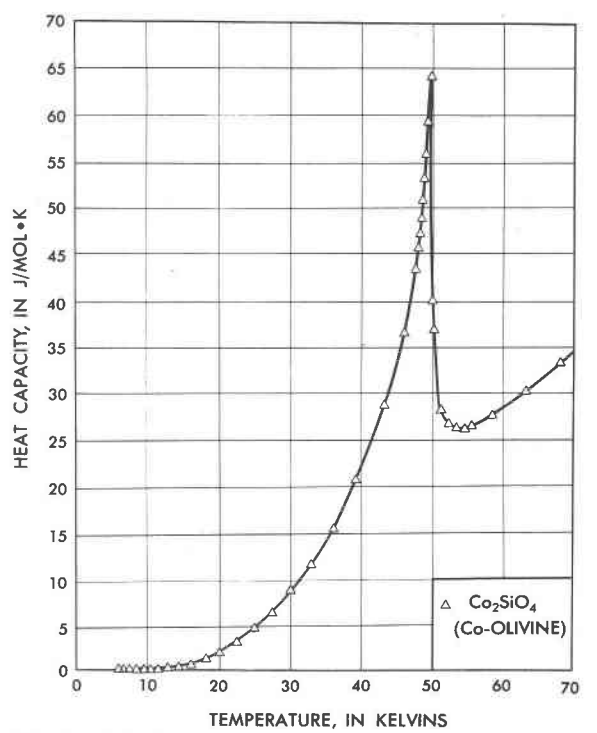

Fig. 3. Molar heat capacity of Co_2SiO_4 in the region of the paramagnetic–antiferromagnetic transition, T_N = 49.76±0.02K.

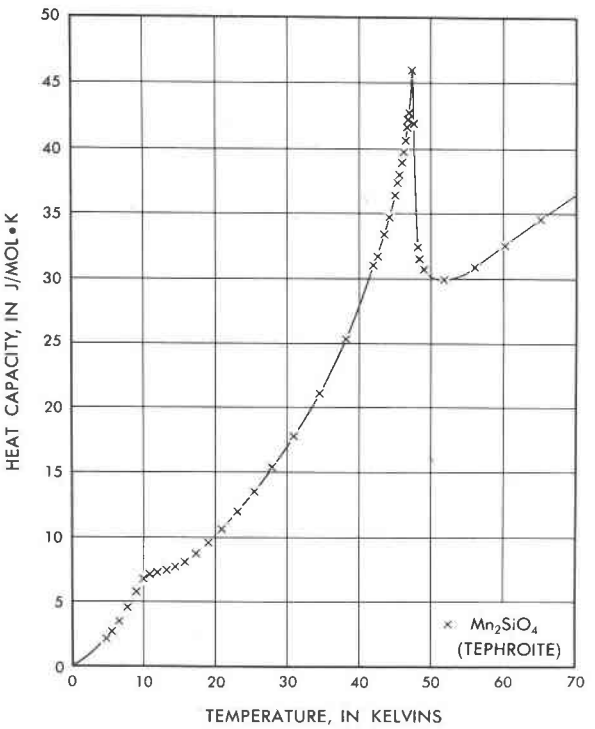

Fig. 4. Molar heat capacity of Mn_2SiO_4 in the region of the low temperature spin ordering transition, 47.38±0.05K.

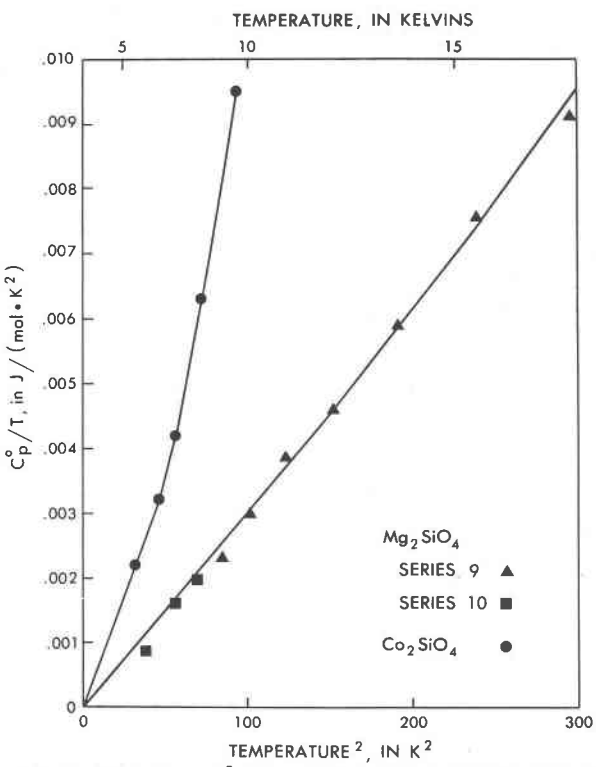

Fig. 5. Cp/T versus T^2 extrapolation of heat capacity data on Mg_2SiO_4 and Co_2SiO_4 to 0 K.

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

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ-S_0^\circ)$	$(H_T^\circ-H_0^\circ)/T$	$-(G_T^\circ-H_0^\circ)/T$
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	1.809	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	111.8	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° 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}°, 94.11±.10 J/(mol·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° 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^{-1}.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ-S_0^\circ)$	$(H_T^\circ-H_0^\circ)/T$	$-(G_T^\circ-H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	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^{-1}.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ-S_0^\circ)$	$(H_T^\circ-H_0^\circ)/T$	$-(G_T^\circ-H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	0.0050	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;

$$C_p = 87.36 + 0.08717T - 3.699\times10^6T^{-2} + 843.6T^{-0.5} - 2.237\times10^{-5}T^2$$

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

The enthalpy change for the reaction

$$2MgO + SiO_2 = Mg_2SiO_4 \qquad (1)$$

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 ± 4.2 kJ for ΔH°_{965} (1) by molten salt calorimetry. Her value is however based on an *estimated* value for ΔH_{soln} of MgO in the molten $2PbO\cdot B_2O_3$ used to dissolve Mg_2SiO_4 and SiO_2. This *estimated* value for ΔH_{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. Charlu *et al.* (1975) obtained -62.6 ± 1.1 kJ at 970 K and Kiseleva *et al.* (1979) obtained -58.2 ± 1.4 kJ for ΔH°_{973} 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 $\Delta H^\circ_{298} = -56.5$ kJ, and is in excellent agreement with that adopted by Robie *et al.* (1979, p. 364), $\Delta H^\circ_{298} = -56.7\pm.7$ kJ/mol which we believe is the best

Table 8. Thermodynamic properties of Mg_2SiO_4 at high temperature and ΔH° and ΔG° for the reaction $2MgO + SiO_2 = Mg_2SiO_4$.

TEMP.	$(H_T-H_{298})/T$	S_T°	$-(G_T-H_{298})/T$	C_p°	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	-55.62	-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 $\Delta H^\circ_{f,298} = -2170.4\pm1.4$ 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 $\Delta G^\circ_{f,298} = -2051.0\pm1.4$ kJ/mol.

The heat capacity equation for forsterite was combined with the value of $\Delta H^\circ_{r,298}$ adopted above and the high temperature thermodynamic functions for periclase and quartz tabulated by Robie *et al.* (1979) to obtain the values of ΔH°_T and ΔG°_T listed in Table 8. Our values for ΔG°_T 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 percent greater at 50 K and decreasing to +0.7 percent 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° data with the heat content measurements of Christensen (Mah, 1960) to generate

$$C_p^\circ = 261.28 - 1.378\times10^{-2}T - 2217.7T^{-0.5} \quad (298\text{–}1600\ \text{K})$$

for Mn_2SiO_4.

Jeffes *et al.* (1954) obtained $\Delta H^\circ_{298} = -49.2\pm2.9$ kJ for the reaction

$$\underset{\text{manganosite}}{2MnO} + \underset{\alpha\text{-quartz}}{SiO_2} \rightleftarrows \underset{\text{tephroite}}{Mn_2SiO_4} \qquad (2)$$

by HF(aq) solution calorimetry (at 25°C). Hemingway and Robie (1977) adjusted this result to -47.1 ± 3.0 kJ to account for the very fine particle size of the quartz used in the ΔH_{sol} measurements. Navrotsky and Coons (1976) obtained $\Delta H^\circ_{298} = -48.5\pm1.4$ kJ for this reaction using molten $2PbO\cdot B_2O_3$ as the solvent. Schwerdtfeger and Muan (1966) give -43.5 ± 1.7 kJ for the Gibbs free energy change, ΔG°_r, for this reaction at 1423 K based on measurements of the equilibrium gas ratios of CO/CO_2 coexisting with phases in the "FeO"–MnO–SiO_2 system. Biggers and Muan (1967) obtained $\Delta G^\circ_{r,1523} = -42.3\pm3.4$ kJ from equilibrium measurements of the exchange reaction

$$CoSiO_3 + 1/2\ Mn_2SiO_4 \rightleftarrows MnSiO_3 + 1/2\ Co_2SiO_4 \qquad (3)$$

combined with the ΔG° values for Co_2SiO_4 from Lebedev *et al.* (1962) and Aukrust and Muan (1963).

Using ΔG°_r from Schwerdtfeger and Muan, and Biggers and Muan, and our heat capacity (and entropy) data together with those for MnO and SiO_2 tabulated by Robie *et al.* (1979) we can also obtain a value for ΔH°_{298} for reaction (2) as follows: from the heat capacity data, we obtain $\Delta S^\circ_{r,1423}$ and from the relation

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

we get $\Delta H^\circ_{r,1423}$ and using Kirchoff's relation calculate $\Delta H^\circ_{r,298} = -53.7\pm2.1$ kJ from Schwerdtfeger and Muan and -53.5 ± 4.4 kJ, from Biggers and Muan respectively. Schreiber (1963) studied the reaction

$$2MnCO_3 + SiO_2 \leftrightharpoons Mn_2SiO_4 + 2CO_2 \qquad (4)$$

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 $\Delta G^\circ_{700} = -44.2$ kJ/mol for the formation of Mn_2SiO_4 from the oxides, and -49.3 kJ/mol for ΔH°_{700} (2).

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

rounded average for $\Delta H^\circ_{r,298}$ (2) of -50.8 ± 2.5 kJ/mol. We combined this value with ancillary data from Robie *et al.* (1979) to obtain -1732.0 ± 2.9 and -1631.5 ± 3.0 kJ/mol for $\Delta H^\circ_{f,298}$ and $\Delta G^\circ_{f,298}$ respectively. In Table 9 we list the high temperature thermodynamic properties for tephroite together with ΔH°_T and ΔG°_T for reaction (2).

Co_2SiO_4

There are apparently no high temperature heat capacity data for Co_2SiO_4. At 298.15 K ΔS° is -4.8 ± 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 α–β transition in quartz. Our estimated heat capacities for Co_2SiO_4 are represented by the equation

$$C^\circ_p = 343.9 - 0.1006T + 3.814\times10^{-5}T^2 - 3175T^{-0.5} \quad (289\text{–}1500\ \text{K})$$

This equation was used together with our measured entropy at 298.15 K to calculate S°_T and H°_T–H°_{298} 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 $\Delta H^\circ_{965} = -21.6\pm2.1$, and $\Delta^\circ_{986} = -23.0\pm0.8$ kJ respectively, for the reaction

$$2CoO + SiO_2 = Co_2SiO_4 \qquad (5)$$

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 1423K, and by Aukrust and Muan (1963) (1273–1573 K) by CO reduction equilibria, and by Kozlowska-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

$$Co_2SiO_4 + 2CO = 2Co + SiO_2 + 2CO_2 \qquad (6)$$

over the temperature range 1083 to 1573 K. To the experimental ΔG°_T data of Lebedev *et al.* for (5) we added ΔG°_T for the reaction

Table 9. Thermodynamic properties of Mn_2SiO_4 at higher temperatures and ΔH° and ΔG° for the reaction $2MnO + SiO_2 = Mn_2SiO_4$.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_p	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	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

$$2Co + 2CO_2 = 2CoO + 2CO \qquad (7)$$

using data from Robie *et al.* (1979) for SiO_2 and the JANAF Thermochemical Tables for CoO to obtain ΔG°_T (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 $\Delta G^\circ_{f,T}$ for CO taken from Richardson and Jeffes (1949) which are incorrect. Aukrust and Muan (1963) obtained their ΔG°_T values for (5) by combining their equilibrium constants for (6) with their own measurements for (7). ΔG°_T for reaction (5) from the CO reduction equilibrium studies are in reasonable agreement but are ≈3 KJ more negative than the ΔG° obtained from the emf measurements. A third-law treatment of these data leads to ΔH°_{298} for reaction (5) of -23.0 ± 1.5 kJ. Combining our values with $\Delta H^\circ_{f,298}$ for CoO and SiO_2 from JANAF (1971) or Robie *et al.* (1979), we obtain $\Delta G^\circ_{f,298} = -1305.8\pm3.0$ kJ/mol and $\Delta H^\circ_{f,298} = -1411.6\pm2.9$ kJ/mol for Co_2SiO_4 (from the elements).

At 975 K, the mean temperature of the molten salt calorimetric determination of ΔH° 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

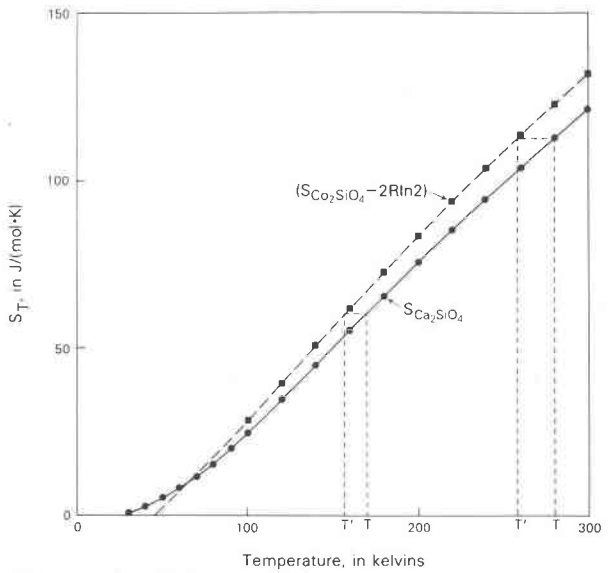

Fig. 6. Plot of the entropy of γ-Ca_2SiO_4 and the quantity $S_{Co_2SiO_4} - 2R\ln 2$.

states model suggested by Stout and Catalano (1955). We used both our C_p° data for Mg_2SiO_4 and those of King (1957) for γ-Ca_2SiO_4 with the corresponding states model to estimate the *lattice* entropies of Mn_2SiO_4 and Co_2SiO_4.[1]

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 γ-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° of γ-Ca_2SiO_4 is the same as C_p° for Mg_2SiO_4 at the temperature T. The ratio T/T' was then plotted as a function of temperature and extropolated to zero kelvin. From the extrapolated values of T/T' and our measured value of C_p° (T) of Mg_2SiO_4 we generated values of C_p° for γ-Ca_2SiO_4 for temperatures between 5 and 52 K. These estimated values for C_p° of γ-Ca_2SiO_4 were combined with King's measured values above 52 K to calculate S_T° for γ-Ca_2SiO_4 at 5 K intervals. Next we plotted S_T° for γ-Ca_2SiO_4 and the quantity $(S_{T_{meas.}}^\circ - 2R1n6)$ for Mn_2SiO_4 where 2R1n6 is the limiting value for the magnetic entropy at high temperature, and derived the ratio T/T' where again T' is the temperature at which the quanity $(S_T^\circ - 2R1n6)$ for Mn_2SiO_4 has the same value as S° (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 Duyneveldt, 1977, p. 64–71) and accordingly for our corresponding states estimation of the lattice entropy we used the quantity $(S_T^\circ - 2R1n2)$ for Co_2SiO_4. We therefore expect the magnetic entropy of Co_2SiO_4 to approach 2R1n2 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 2R1n6 (29.79 J/mol·K) at the Néel temperature, and that of Co_2SiO_4 is only about 71 percent of 2R1n2 (11.53 J/

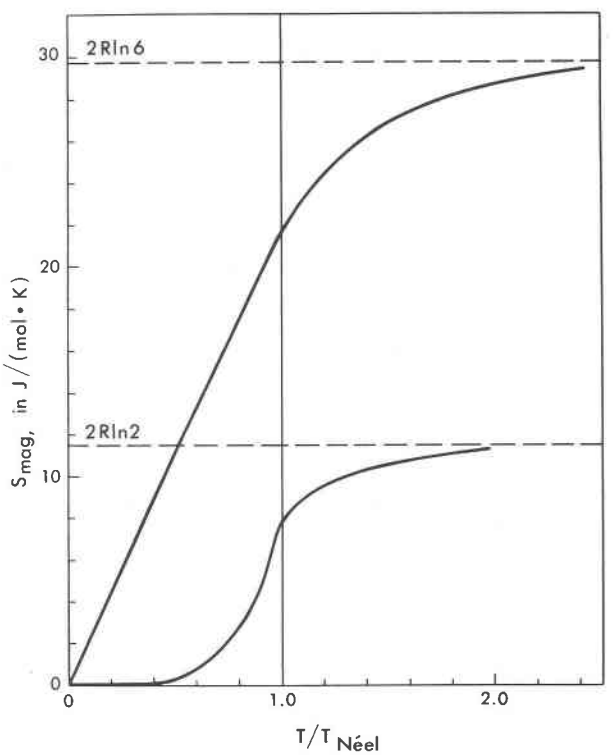

Fig. 7. Magnetic entropies of Co_2SiO_4 and Mn_2SiO_4.

[1]Although neither Mg_2SiO_4 or γ-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).

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, θ_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 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 (6.62618×10^{-34} J·sec), k is Boltzman's constant (1.38066×10^{-23} J·K^{-1}), q is the number of atoms in the "molecule", N is Avogadro's number (6.02209×10^{23} mol^{-1}), ρ is the density in g · cm^{-3}, 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 $\theta_D^E(0) =$

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

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 (θ_D^C) 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 θ_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)

$$C_V = [12/5\ \pi^4 qRT^3]/\theta_D^3 \qquad (10)$$

for $T < \theta_D/50$. This calculated lattice heat capacity is then substracted 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°.

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.

References

Aukrust, E., and Muan, A. (1963) The stabilities of $CoO{\cdot}Al_2O_3$, $CoO{\cdot}Cr_2O_3$, and $2CoO{\cdot}SiO_2$. Journal of the American Ceramic Society, 46, 358.

Biggers, J.V., and Muan, A. (1967) Activity–composition relations in orthosilicate and metasilicate solid solutions in the system MnO-CoO-SiO_2. Journal of the American Ceramic Society, 50, 230–235.

Blackman, M. (1955) The specific heat of solids. In S. Flugge, Ed., Encyclopedia of Physics, p. 325–382. Springer-Verlag, Berlin.

Carlin, R.L., and van Duyneveldt, A.J. (1977) Magnetic properties of transition metal compounds. Springer-Verlag, New York, New York.

Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO–Al_2O_3–SiO_2 from high temperature solution calorimetry. Geochimica et Cosmochimica Acta, 39, 1487–1497.

Fujino, K., Saski, S., Takeuchi, Y., and Sadanaga, R. (1981) X-ray determination of electron distributions in forsterite, fayalite and tephroite. Acta Crystallographica, B37, 513–518.

Gopal, E.S.R. (1966) Specific heats at low temperatures. Plenum Press, New York.

Graham, E.K., and Barsch, G.R. (1969) Elastic constants of single crystal forsterite as a function of temperature and pressure. Journal of Geophysical Research, 74, 5949–5960.

Hazen, R.M. (1976) Effect of temperature and pressure on the crystal structure of forsterite. American Mineralogist, 61, 1280–1293.

Hemingway, B.S. and Robie, R.A. (1977) Enthalpies of formation of low albite ($NaAlSi_3O_8$), gibbsite ($Al(OH)_3$), and $NaAlO_2$; revised values for $\Delta H^\circ_{f,298}$ and $\Delta G^\circ_{f,298}$ of some aluminosilicate minerals. Journal of Research of The U.S. Geological Survey, 5, 413–429.

Jeffes, J.H., Richardson, F.D., and Pearson, J. (1954) The heat of formation of manganous orthosilicate and manganous sulfide. Transactions of the Faraday Society, 50, 364–370.

Kelley, K.K. (1943) Specific heats at low temperatures of magnesium orthosilicate, and magnesium metasilicate. Journal of the American Chemical Society, 65, 339–341.

Kiseleva, I.A., Ogorodova, L.P., and Topor, N.P. (1979) Determination of the heat of dissolution of magnesium oxide by a high-temperature calorimetric method. Vestnik Moskovskogo Universiteta Seriia 2, Khimia, 20, 243–247. [Chemical Abstracts, 91, 97622a]

King, E.G. (1957) Low temperature heat capacities and entropies at 298.15 K of some crystalline silicates containing calcium. Journal of the American Chemical Society, 79, 5437–5438.

King, E.G., Barany, R. and Weller, W.W. (1967) Thermodynamic properties of forsterite and serpentine. U.S. Bureau of Mines Report of Investigations, 6962.

Kozlowska-Rog, A., and Rog, G. (1979) Thermodynamics of zinc and cobalt silicates. Polish Journal of Chemistry, 53, 2083–2086.

Lebedev, B.G., Levitskii, V.A., and Burtstev, V.A. (1963) Equilibrium in reduction of cobalt orthosilicate by carbon monoxide. Russian Journal of Physical Chemistry, 36, 460–461.

Mah, A.D. (1960) Thermodynamic properties of manganese and its compounds. U.S. Bureau of mines Report of Investigations, 5600.

Morimoto, N., Tokonami, M., Watanabe, M., and Koto, K. (1974) Crystal structure of three polymorphs of Co_2SiO_4. American Mineralogist, 59, 475–485.

Narvrotsky, A. (1971) Thermodynamics of formation of the silicates and germanates of some divalent transition metals and of magnesium. Journal of Inorganic and Nuclear Chemistry, 33, 4033–4050.

Navrotsky, A., and Coons, W.E. (1976) Thermochemistry of some pyroxenes and related compounds. Geochimica et Cosmochimica Acta, 40, 1281–1288.

Navrotsky, A., Pintchovski, F.S., and Akimoto, S. (1979) Calorimetric study of the stability of high pressure phases in the systems CoO–SiO_2 and "FeO"–SiO_2 and calculation of the phase diagrams in MO–SiO_2 systems. Physics of the Earth and Planetary Interiors, 19, 275–292.

Nomura, S., Santoro, R.P., Fang, J., and Newnham, R.E. (1964) Antiferromagnetism in cobalt orthosilicate. Journal of Physics and Chemistry of Solids, 25, 901–925.

Orr, R.L. (1953) High temperature heat contents of magnesium orthosilicate and ferrous orthosilicate. Journal of the American Chemical Society, 75, 528–529.

Osborne, D.W., Flotow, H.E., and Schreiner, F. (1967) Calibration and use of germanium resistance thermometers for precise

heat capacity measurements from 1 to 25°K, high purity copper for inter-laboratory heat capacity comparisons. Review of Scientific Instruments, 38, 159–168.

Richardson, F.D. and Jeffes, J.H.E. (1949) The thermodynamic background of iron and steel making processes. I. The blast furnace. Journal of the Iron and Steel Institute, 163, 397–420.

Robie, R.A., and Edwards, J.L. (1966) Some Debye temperatures from single-crystal elastic constant data. Journal of Applied Physics, 37, 2659–2663.

Robie, R.A. and Hemingway, B.S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. U.S. Geological Survey Professional Paper 755.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452.

Robie, R.A., Hemingway, B.S., and Wilson, W.H. (1976) The heat capacities of Calorimetry Conference copper and of muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, and illite $K_3(Al_7Mg)(Si_{14}Al_2)O_{40}(OH)_8$ between 15 and 374 K and their standard entropies at 298.15 K. Journal of Research of the U.S. Geological Survey, 4, 631–644.

Rog, G., Langanke, B., Borcherdt, G., and Schmalzried, H. (1974) Determination of the standard Gibbs free energies of formation of the silicates of cobalt, magnesium, and strontium by e.m.f. measurements. Journal of Chemical Thermodynamics, 6, 1113–1119.

Ross, C.S., Foster, M.D., and Meyers, A.T. (1954) Origin of dunites and of olivine-rich inclusions in basaltic rocks. American Mineralogist, 39, 693–737.

Santoro, R.P., Newnham, R.E., and Nomura, S. (1966) Magnetic properties of Mn_2SiO_4 and Fe_2SiO_4. Journal of Physics and Chemistry of Solids, 27, 655–666.

Schreiber, E. (1963) The equilibrium boundary for the reaction $2MnCO_3 + SiO_2 \rightleftarrows Mn_2SiO_4 + 2CO_2$. Ph.D. Thesis, State University of New York, Alfred.

Schwerdtfeger, K., and Muan, A. (1966) Activities in olivine and pyroxenoid solid solutions of the system Fe–Mn–Si–O at 1150°C. Transactions of the Metallurgical Society of AIME, 236, 201–211.

Stout, J.W., and Catalano, E. (1955) Heat capacity of zinc fluoride from 11 to 300°K. Thermodynamic functions of zinc fluoride. Entropy and heat capacity associated with the antiferromagnetic ordering of manganous fluoride, ferrous fluoride, cobaltous fluoride and nickelous fluoride. Journal of Chemical Physics, 23, 2013–2022.

Sumino, Y. (1979) The elastic constants of Mn_2SiO_4, Fe_2SiO_4 and Co_2SiO_4, and the elastic properties of olivine group minerals at high temperature. Journal of Physics of the Earth, 27, 209–238.

Sumino, Y., Nishizawa, O., Goto, T., Ohno, I. and Ozima, M. (1977) Temperature variation of elastic constants of single crystal forstenite between 190° and 400°C. Journal of Physics of the Earth, 25, 377–392.

Syono, Yasuhiko, Akimoto, Syun-iti, and Matsui, Yoshito (1971) High pressure transformation in zinc silicates. Journal of Solid State Chemistry, 3, 369–380.

Takei, Humihiko (1976) Czochralski growth of Mn_2SiO_4 (tephroite) single single crystal and its properties. Journal of Crystal Growth, 34, 125–131.

Takei, Humihiko (1978) Growth of fayalite (Fe_2SiO_4 single crystals by the floating zone method. Journal of Crystral Growth, 43, 463–468.

Takei, Humihiko and Kobayashi, Takaaki (1974) Growth and properties of Mg_2SiO_4 single crystals. Journal of Crystal Growth, 23, 121–124.

Torgeson, D.R., and Sahama, T.G. (1948) A hydrofluoric acid solution calorimeter and the determination of the heats of formation of Mg_2SiO_4, $MgSiO_3$, and $CaSiO_3$. Journal of the American Chemical Society, 70, 2156–2160.

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