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Heat capacity and entropy of Ni_2SiO_4-olivine from 5 to 1000 K and heat capacity of Co_2SiO_4 from 360 to 1000 K

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Abstract

The heat capacity of Ni_2SiO_4-olivine has been measured between 5 and 387 K by cryogenic adiabatic-shield calorimetry and between 360 and 1000 K by differential scanning calorimetry. There is a λ-type transition in Ni_2SiO_4-olivine at 29.15±0.05 K. At 298.15 K the molar heat capacity and entropy of Ni_2SiO_4-olivine are 123.2±0.2 and 128.1±0.2 J/(mol · K), respectively. Between 300 and 1300 K the heat capacity can be represented by the equation $C_P^\circ = 289.73 - 0.024015T + 131045/T^2 - 2779.0/T^{1/2}$ to within ±0.5%. From our heat capacity measurements, combined with results from molten salt calorimetry, thermal decomposition of Ni_2SiO_4-olivine into its constituent oxides, and equilibrium studies, both by CO reduction and solid state electrochemical cell measurements for the reaction

$$2Ni + SiO_2 + O_2 = Ni_2SiO_4,$$

we calculate that $\Delta G^\circ_{f,298} = -1289.0\pm3.1$ and $\Delta H^\circ_{f,298} = -1396.5\pm3.0$ kJ/mol. Our data when coupled with the extant molar volume and phase boundary data yield $S^\circ_{298} = 124.1\pm0.4$ J/(mol · K) and $\Delta G^\circ_{f,298} = -1281\pm3.5$ kJ/mol for Ni_2SiO_4-spinel.

The heat capacity of Co_2SiO_4-olivine was also measured between 360 and 1000 K by differential scanning calorimetry. Our data are represented by $C_P^\circ = 305.83 - 0.031952T + 269254/T^2 - 2865.2/T^{1/2}$ to ±0.8 percent for the temperature range 300–1300 K.

Introduction

Ni_2SiO_4 has the olivine structure at one bar pressure (Brown, 1970) and forms a continuous series of solid solutions with Mg_2SiO_4 (forsterite) (Ringwood, 1956). It has been much studied at high pressures because it transforms into the spinel polymorph at pressures that are much lower than those required for Mg_2SiO_4 and therefore serves as a model for a phase transition in the upper mantle. Ni_2SiO_4-olivine occurs in nature as the mineral liebenbergite. (De Waal and Calk, 1973).

Previous thermochemical measurements on Ni_2SiO_4-olivine include a value for the enthalpy of the reaction $2NiO + SiO_2 = Ni_2SiO_4$ at 965 K (Navrotsky, 1971), heat capacity measurements between 350 and 700 K by Watanabe (1982), and measurements of the equilibrium constant as a function of temperature by solid state electrochemical cell studies by Taylor and Schmalzried (1964), and by carbon monoxide reduction by Lebedev and Levitskii (1961), Burdese, Abbattista, and Damiani (1963), and Campbell and Roeder (1968) for the equilibrium

$$2Ni + SiO_2 + O_2 = Ni_2SiO_4\text{-olivine}.$$

These several equilibrium measurements differ significantly. We have combined our measurements of the heat capacity and entropy of Ni_2SiO_4-olivine with existing phase equilibrium studies to calculate the Gibbs free energies of formation of Ni_2SiO_4-olivine and Ni_2SiO_4-spinel.

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Low-temperature heat capacity measurements and the entropy of Co_2SiO_4 have been previously reported from this laboratory (Robie, Hemingway, and Takei, 1982). Watanabe (1982) has measured the heat capacity of Co_2SiO_4 from 350 to 700 K. However, the heat capacities reported by Watanabe (1982) for Ni_2SiO_4 and Co_2SiO_4 are 4.6 and 2.5%, respectively, larger than the heat capacities obtained with the more accurate low-temperature calorimeter. New measurements for C_P° between 350 and 1000 K are presented here.

Procedure for the growth of nickel-olivine crystals

Phase equilibrium studies of the system NiO–SiO_2 by Phillips et al. (1963) showed that Ni_2SiO_4-olivine decomposed above 1818 K to bunsenite (NiO), and cristobalite (SiO_2). High-temperature solvents (fluxes) have been widely used to grow crystals at subsolidus temperatures. For the present experiments, we used sodium tungstate, Na_2WO_4, although the solubility of nickel olivine in this solvent is not especially high. Preliminary studies showed that excess SiO_2 had to be added in the melt because SiO_2 was more soluble than NiO in the solvent. The initial starting composition for the melt and slow cooling experiments was $NiCO_3$ = 12.0 g, SiO_2 = 3.47 g and $Na_2WO_4 \cdot H_2O$ = 69 g which yielded approximately 8 g of relatively inclusion-free single crystals of Ni_2SiO_4-olivine. This composition represents a mole ratio for NiO:SiO_2 of 1.73:1.0.

Platinum crucibles of 50 ml capacity each containing the above charge were placed in a globar (silicon carbide) furnace and heated at 1553 K for 5 days for equilibration. This long period of soaking was necessary because of the slow reaction rate of the charges at this temperature, and relatively low solubility of Ni_2SiO_4-olivine in the solvent. The melt was then cooled slowly at 2 K per hour down to 1023 K using a programmed proportional controller.

As the temperature of the melt decreased, spontaneous nucleation by supersaturation of the melt took place primarily at the bottom and lower walls of the crucibles, because of a temperature gradient that made the bottom of the crucibles cooler. Crystals then grew continuously inward. Although the specific gravity of Ni_2SiO_4-olivine, 4.92 g/cm^3, is greater than that of the solvent, 4.18 g/cm^3, some crystals were found on the surface of the melt.

The crucible was removed from the furnace after it had cooled to near room temperature. Excess Na_2WO_4 was readily dissolved in 400 ml of hot 2% ammonia solution in a glass beaker. Coarse aggregates were crushed gently in an agate mortar and washed. The unwanted residue, consisting of white amorphous matter, silica compounds, fine-grained Ni_2SiO_4-olivine and glassy round globules was removed by density separation by flushing off with tap water in a porcelain evaporating dish. The dried products were sieved and the material passing a 120 mesh sieve (0.125 mm) discarded. Examination under a binocular microscope (37.5×) indicated the absence of any trapped flux. Unit-cell parameters for this material have been determined by Brown (1970, 1980).

Experimental heat capacities of Ni_2SiO_4-olivine

Our experimental low-temperature heat capacity values are listed in their chronological order of measurement in Table 1. The measurements of series 1 through 12 were made in May 1977. The calorimeter contained 49.028 g (in vacuum) of Ni_2SiO_4. Several modifications were then made to the calorimetric system. A sample of 47.642 g of Ni_2SiO_4 was reloaded into the calorimeter and the data of series 1a through 7a made in March 1979. The values in

Table 1. Experimental molar heat capacities of Ni_2SiO_4-olivine made with adiabatically shielded calorimeter

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 6		Series 1a	
6.19	1.251	138.26	64.92	5.38	0.693
6.25	1.368	144.11	68.04	6.45	1.174
7.36	1.676	150.21	71.19	7.52	1.744
8.53	2.325	156.49	74.21	8.75	2.433
9.62	2.948	162.75	77.24	9.94	3.115
10.69	3.568	168.95	80.29	11.16	3.806
11.84	4.194	175.06	83.04	12.45	4.512
13.11	4.890	181.06	85.69	13.89	5.321
14.54	5.722	187.16	88.16	15.67	6.352
16.17	6.654	193.45	90.71	17.87	7.720
17.96	7.790	199.61	92.97	20.14	9.392
19.86	9.182	205.66	95.34	22.49	11.51
21.97	10.98	211.63	97.74	24.94	14.41
24.25	13.49	Series 7, 8		27.08	17.89
26.65	17.12	217.05	99.70	28.23	20.44
*29.56	16.43	223.31	101.9	28.50	21.29
33.60	11.62	229.85	104.2	28.71	22.14
37.64	12.14	236.23	106.2	28.95	23.54
45.22	14.12	242.96	108.3	29.11	24.85
49.96	15.80	250.12	110.7	Series 2a	
55.32	18.07	257.15	112.6	28.55	21.47
Series 2		264.07	114.5	28.73	22.23
25.40	15.01	270.90	116.3	28.90	23.20
26.02	15.97	277.65	118.2	29.03	24.15
26.75	17.20	284.34	119.8	29.12	24.85
27.48	18.25	290.95	121.6	29.20	23.29
28.08	20.06	Series 9		29.34	16.47
28.43	21.13	295.98	122.8	30.37	12.32
28.65	21.91	302.02	124.2	32.94	11.56
28.87	23.98	308.33	125.5	36.26	11.89
29.03	24.24	314.95	127.0	39.80	12.60
*29.13	24.99	321.53	128.6	43.72	13.67
29.31	17.86	328.05	129.9	47.72	14.98
29.59	13.68	Series 10		Series 3a	
29.95	12.59	333.98	131.0	87.97	35.82
30.37	12.06	340.49	132.4	93.27	38.98
30.79	11.79	346.88	133.7	98.59	42.16
31.21	11.65	353.51	134.8	104.23	45.51
31.74	11.55	Series 11, 12		Series 4a	
Series 3		360.35	135.7	157.87	74.80
52.55	16.91	367.20	137.0	163.76	77.60
57.28	19.02	374.03	138.2	169.59	80.33
62.08	21.28	380.80	139.5	175.56	83.03
67.42	24.01	387.54	140.3	Series 5a	
72.65	26.88			215.75	99.07
77.61	29.71			221.29	101.0
82.48	32.64			227.15	103.0
Series 4, 5				233.10	105.0
82.40	32.63			Series 6a	
87.20	35.40			280.61	118.8
91.82	38.21			286.29	120.3
96.37	40.89			292.05	121.8
101.04	43.68			297.77	123.0
105.94	46.64			Series 7a	
111.06	49.67			330.91	130.3
116.31	52.73			336.30	131.3
121.62	55.80				
126.98	58.87				
132.59	61.94				

* Temperature rise straddled the maximum in C_P°

Table 1 refer to a formula weight of 209.483 gram/mol and the temperatures are on the International Practical Temperature Scale of 1968 (IPTS-68).

Ni_2SiO_4-olivine has a pronounced λ-type transition at 29.15±0.05 K. This arises from the antiferromagnetic ordering of the magnetic moments of the Ni^{2+} ions as the temperature is decreased. Our value for the Néel temperature is 4.85 K lower than that obtained by Newnham et al. (1965) by magnetic susceptibility measurements on a powdered sample using a vibrating sample magnetometer. Our experimental data in the neighborhood of the Néel temperature are shown in Figure 1 and were extrapolated graphically to 0 K. Above 35 K, the data were smoothed using the smoothing spline procedure discussed by Robie, Finch, and Hemingway (1982). The apparatus used and other experimental procedures are discussed elsewhere (Robie and Hemingway, 1972, Robie et al., 1976).

Thermodyamic properties of Ni_2SiO_4

Smoothed values for the thermodynamic functions C°_P, $S^\circ_T - S^\circ_0$, $(H^\circ_T - H^\circ_0)/T$, and $(G^\circ_T H^\circ_0)/T$ derived from these data are given in Table 2 at integral temperatures to 380 K. At 298.15 K, the heat capacity and entropy change for Ni_2SiO_4-olivne are 123.2±0.2 and 128.1±0.2 J/(mol · K), respectively. There is no cation disorder in Ni_2SiO_4-olivine therefore $S^\circ_0 = 0$.

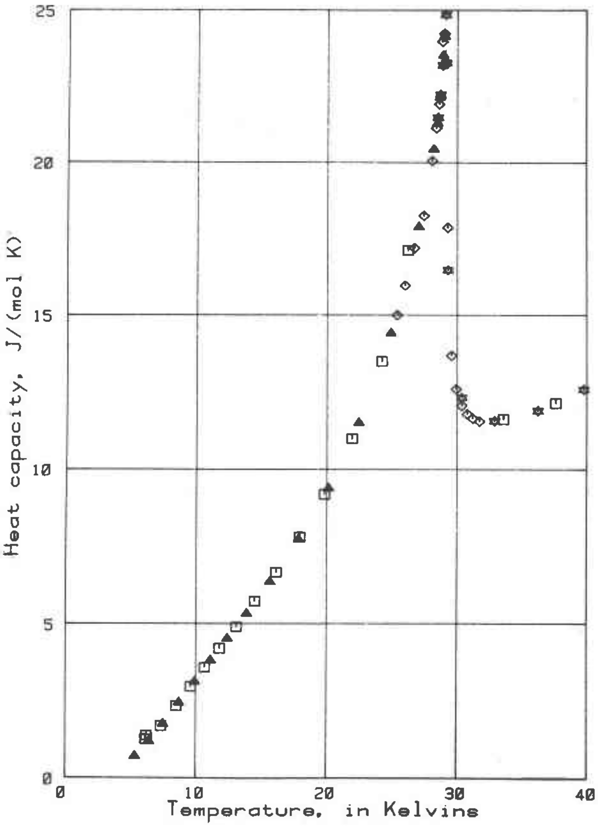

Fig. 1. Experimental molar heat capacities of Ni_2SiO_4-olivine in the neighborhood of the Néel temperature. Open rectangles, series 1; open diamonds, series 2; solid triangles, series 1a; open stars, series 2a.

Table 2. Molar thermodynamic properties of Ni_2SiO_4-olivine (Formula weight = 209.483 g/mol)

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C°_P	$S^\circ_T - S^\circ_0$	$(H^\circ_T - H^\circ_0)/T$	$-(G^\circ_T - H^\circ_0)/T$
Kelvin	J/(mol·K)			
5	1.459	0.549	0.390	0.159
10	3.144	1.350	0.960	0.390
15	5.961	3.154	2.154	1.000
20	9.269	5.293	3.494	1.799
25	14.50	7.867	5.121	2.746
30	17.72	11.11	7.241	3.869
35	11.67	14.72	9.564	5.156
40	12.62	16.35	9.892	6.454
45	14.02	17.91	10.27	7.640
50	15.84	19.48	10.73	8.745
60	20.26	22.74	11.94	10.80
70	25.42	26.24	13.49	12.76
80	31.14	30.01	15.33	14.67
90	37.08	34.02	17.42	16.60
100	43.05	38.23	19.68	18.55
110	49.01	42.62	22.08	20.54
120	54.86	47.13	24.57	22.57
130	60.50	51.75	27.12	24.63
140	65.88	56.43	29.70	26.74
150	71.02	61.15	32.28	28.87
160	75.92	65.89	34.86	31.04
170	80.64	70.64	37.41	33.23
180	85.11	75.38	39.94	35.44
190	89.30	80.09	42.43	37.66
200	93.25	84.77	44.87	39.90
210	97.04	89.42	47.27	42.15
220	100.7	94.01	49.61	44.40
230	104.1	98.56	51.91	46.66
240	107.4	103.1	54.15	48.92
250	110.5	107.5	56.34	51.17
260	113.4	111.9	58.48	53.42
270	116.1	116.2	60.57	55.67
280	118.7	120.5	62.60	57.91
290	121.3	124.7	64.58	60.14
300	123.7	128.9	66.51	62.36
310	126.0	133.0	68.39	64.57
320	128.1	137.0	70.22	66.77
330	130.2	141.0	72.01	68.96
340	132.2	144.9	73.75	71.14
350	134.1	148.7	75.45	73.30
360	135.8	152.5	77.10	75.45
370	137.5	156.3	78.71	77.58
380	139.2	160.0	80.28	79.70
273.15	117.0	117.6	61.21	56.38
298.15	123.2	128.1	66.15	61.95

We have also measured the heat capacity between 350 and 1000 K using a differential scanning calorimeter. The 31.015 mg sample was sealed in a gold pan and was heated at 10 K/min using a sensitivity of 0.02 watts. Our results are listed in Table 3. The results of Watanabe (1982) are systematically 3–4% greater than our values over his range of measurements 350–700 K. They are also 4.6% higher than our values measured with the low-temperature adiabatic calorimeter.

We have combined our heat capacity values above 300 K obtained with the low-temperature calorimeter with our data from the differential scanning calorimeter to

Table 3. Experimental molar heat capacities of Ni_2SiO_4-olivine measured by differential scanning calorimetry

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
360.1	138.1	650.2	165.8
370.1	139.0	660.2	166.5
390.1	142.0	680.2	167.9
410.1	145.6	700.2	168.9
430.1	147.3	720.2	170.0
440.1	148.9	730.2	170.4
		740.2	171.5
420.1	146.5		
430.1	147.4	720.2	168.3
450.1	148.8	730.2	168.9
470.1	151.5	750.3	169.8
490.1	153.1	770.3	169.8
510.1	154.1	790.3	170.8
520.2	156.4	800.3	171.4
420.0	147.3	760.3	171.1
430.0	147.7	770.3	171.6
450.0	150.2	780.3	171.3
470.0	152.7	800.3	172.7
490.0	153.9	.810.3	173.7
510.0	156.5		
520.0	157.5	850.2	173.7
		860.1	173.0
500.1	153.6	909.3	174.5
510.1	154.6	919.3	175.5
530.1	157.6		
550.1	158.0	909.5	172.9
570.1	159.4	929.4	175.6
590.1	159.2	939.3	176.2
600.1	159.5	949.2	177.0
580.2	159.6	949.2	176.6
590.2	160.9	959.1	177.4
610.2	163.8	969.0	178.1
630.2	163.3		
650.2	163.4	958.9	178.0
		968.8	178.2
		978.7	178.2
		988.6	177.7
		998.4	178.4

generate a preliminary equation for C°_P up to 1000 K. We then used the derivative of this equation, dC°_P/dT, at 950 K to make a linear extrapolation of C°_P to 1300 K. C°_P values taken from this extrapolation at 1050, 1100, 1150, 1200, 1250, and 1300 K were added to the measured data and the combined data set was refit by least-squares yielding, for the range 300 − 1300 K,

$$C^\circ_P = 289.73 - 0.024015T + 131045/T^2 - 2779.0/T^{1/2} \quad (1)$$

This equation fits our data with an average deviation of ±0.5% and was constrained to join smoothly with the values obtained from the more accurate low-temperature calorimeter.

The sample of Co_2SiO_4-olivine was a part of the material used for the low-temperature heat capacity measurements of Robie, Hemingway, and Takei (1982). The sample was in the form of a circular disk polished on the flat surfaces, 6.45 mm diameter by 0.51 mm high and weighed 73.228 mg. Our measurements (360–1000 K) are listed in Table 4. We have combined our heat capacity data with the results of Robie, Hemingway, and Takei (1982) between 300 and 380 K and fit the combined data set by least squares to a 4 term polynomial with the constraint that the equation had to fit the low-temperature C°_P data in the range 300–370 K. The resultant equation is

$$C^\circ_P = 305.83 - 0.031952T + 269254/T^2 - 2865.2/T^{1/2} \quad (2)$$

and fits the high-temperature data with an average deviation of ±0.8%. Watanabe (1982) has also measured the heat capacity of Co_2SiO_4-olivine between 350 and 700 K by differential scanning calorimetry. His results are systematically greater than ours by 2.5% at 350 K increasing to 3.1% at 700 K.

Table 4. Experimental molar heat capacities of Co_2SiO_4 obtained by differential scanning calorimetry

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
360.2	145.4	769.2	179.0
370.1	147.1	779.2	179.6
380.1	148.8	789.1	179.7
390.1	150.5	799.1	179.6
400.1	152.2	809.1	179.4
410.0	153.5	819.1	179.0
420.0	154.8	829.0	179.6
430.0	156.4	839.0	179.7
440.0	157.6	849.0	180.2
449.9	159.0	859.0	180.7
459.9	160.3	868.9	181.3
469.9	161.3	878.9	182.0
479.9	162.4	888.9	184.0
489.8	163.2		
499.8	164.0	789.1	178.5
509.8	164.9	799.1	179.0
519.8	165.7	809.1	178.4
529.8	166.5	819.1	178.4
539.7	167.2	829.0	178.4
547.7	167.7	839.0	178.6
		849.0	178.8
479.9	162.1	859.0	178.9
489.8	163.0	868.9	179.1
499.8	163.9	878.9	181.0
509.8	164.8	888.9	182.1
519.8	165.8	896.9	183.7
529.8	166.7		
539.7	167.5	868.9	179.6
549.7	168.4	878.9	178.5
559.7	169.3	888.9	179.8
569.7	169.9	898.9	178.3
579.6	170.6	908.8	179.5
589.6	171.3	918.8	178.6
597.6	172.1	928.8	179.3
		938.8	179.7
589.6	171.4	948.7	180.1
599.6	171.9	958.7	181.3
609.6	172.4	968.7	184.0
619.5	172.7	978.7	184.7
629.5	173.2	988.7	185.4
639.5	173.8	997.5	187.0
649.5	174.2		
659.4	174.5	868.9	181.6
669.4	174.6	878.9	182.3
679.4	175.1	888.9	182.8
689.4	175.0	898.9	183.2
697.4	175.4	908.8	184.2
		918.8	185.1
689.4	174.8	928.8	184.9
699.3	174.9	938.8	183.6
709.3	175.2	948.7	181.6
719.3	175.9	958.7	180.4
729.3	176.0	968.7	179.4
739.3	176.3	978.7	180.6
749.2	176.8	988.7	181.5
759.2	176.6	997.5	182.2
769.2	177.2		
779.2	177.4		
789.1	178.0		
797.1	178.4		

Gibbs free energy of formation of Ni_2SiO_4-olivine and Ni_2SiO_4-spinel

Phillips et al. (1963) found that Ni_2SiO_4-olivine was unstable relative to NiO and SiO_2 (cristobalite) above 1818 K. From this Observation we calculate $\Delta H^\circ_{298} = 8.72$ kJ for the reaction

$$\underset{\text{olivine}}{Ni_2SiO_4} = \underset{\text{bunsenite}}{2NiO} + \underset{\text{cristobalite}}{SiO_2}$$

and combining this value with the $\Delta H^\circ_{f,298}$ for NiO, and cristobalite from Robie et al. (1979) yields $\Delta H^\circ_{f,298} = -1396.7 \pm 2.2$ kJ/mol for Ni_2SiO_4-olivine. Navrotsky (1971) obtained $\Delta H^\circ_{965} = -13.9 \pm 1.9$ kJ for the reaction

$$\underset{\text{bunsenite}}{2NiO} + \underset{\text{quartz}}{SiO_2} = \underset{\text{olivine}}{Ni_2SiO_4}$$

by molten salt calorimetry. Converting to 298.15 K yields $\Delta H^\circ_{298} = -6.3 \pm 1.9$ kJ from which $\Delta H^\circ_{f,298}$ (Ni_2SiO_4) = -1396.5 ± 2.4 kJ/mol. We have also made a third-law analysis of the high-temperature emf data of Taylor and Schmalzried (1964), and of the CO reduction equilibrium data of Lebedev and Levitskii (1961), Burdese et al. (1963), and of Campbell and Roeder (1968). From these six data sets we have selected $\Delta H^\circ_{f,298} = -1396.5 \pm 3.0$ kJ/mol as the best value for Ni_2SiO_4-olivine.

Using $\Delta H^\circ_{f,298} = -1396.5 \pm 3.0$ kJ/mol, the C°_P for Ni_2SiO_4 from equation (1), and the values of Robie et al. (1979) for Ni, O_2, SiO_2 (quartz and cristobalite) we have calculated ΔG°_T for the reaction

$$2Ni + SiO_2 + O_2 = Ni_2SiO_4\text{-olivine}$$

Our calculated curve is compared in Figure 2 with the experimental measurements on this equilibria by Lebedev and Levitskii (1961), Burdese et al. (1963), Taylor and Schmalzried (1974), and Campbell and Roeder (1968), and with a curve calculated from the equation given by Kother and Muller (1978) for ΔG°_f of Ni_2SiO_4-olivine and the ΔG°_f for NiO from Robie et al. (1979). The data of all but Lebedev and Levitskii (1961) are in satisfactory agreement with the calculated curve.

We have also calculated the entropy and Gibbs free energy of Ni_2SiO_4-spinel. We used the unit-cell data of Finger et al. (1977) and Yagi et al. (1974) for Ni_2SiO_4-spinel, and that of Brown (1970), and Lager and Meagher (1978) for Ni_2SiO_4-olivine together with Deslattes et al. (1974) value for Avogadro's number, $6.022094 \pm 0.000008 \times 10^{23}$ mol^{-1}, to calculate the molar volumes, V°_{298}, of 39.18 ± 0.01 and 42.57 ± 0.02 cm^3 for the spinel and olivine phase, respectively. From our value for the entropy of Ni_2SiO_4-olivine, the above molar volumes, and the slope of the spinel-olivine phase boundary given by Ma (1974) and by Akimoto et al. (1965) we calculate $S^\circ_{298} = 124.1 \pm 0.4$ for the entropy of Ni_2SiO_4-spinel. The phase boundary curves of Akimoto et al. (1965) and Ma (1974) have essentially the same slope, but differ in pressure, for a given temperature, by 4.3 kbar. Using our value for $\Delta G^\circ_{f,298}$ of Ni_2SiO_4-olivine, we calculate $\Delta G^\circ_{f,298}$ for Ni_2SiO_4-spinel = -1282.4 kJ/mol from the data of Akimoto et al., and from the data of Ma, -1281.0 kJ/mol. From the calorimetric data of Navrotsky (1973), $\Delta H^\circ_r = 8.4 \pm 3.4$ kJ/mol for the transition Ni_2SiO_4-olivine = Ni_2SiO_4-spinel; at 298.15 K we calculate -1279.4 kJ/mol for the Gibbs free energy of formation of Ni_2SiO_4-spinel. The uncertainty in the calorimetric ΔH°_{298} of transition corresponds to 10 kbar in the location of the olivine-spinel phase boundary. Our measured and derived values for the thermodynamic properties of the olivine and spinel forms

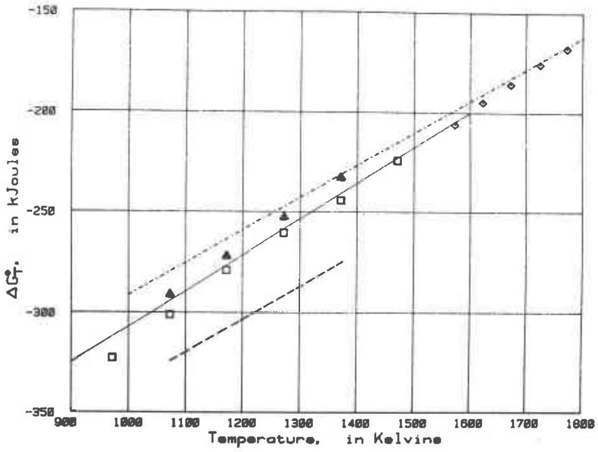

Fig. 2. Change in the Gibbs free energy versus temperature for the reaction $2Ni + SiO_2 + O_2 = Ni_2SiO_4$. Solid triangles, Taylor and Schmalzried (1964); rectangles, Burdese et al. (1963); open diamonds, Campbell and Roeder (1968); dashed line Lebeev and Levitskii (1961); solid line, calculated from calorimetric data; dot–dash line calculated from equation of Kother and Muller (1978).

Table 5. Thermodynamic properties of the olivine and spinel forms of Ni_2SiO_4

Property		Ni_2SiO_4 olivine	Ni_2SiO_4 spinel
S°_{298}	J/(mol·K)	128.1 ± 0.2	124.1 ± 0.4
$\Delta S^\circ_{f,298}$	J/(mol·K)	-360.75 ± 0.28	-364.75 ± 0.45
$\Delta H^\circ_{f,298}$	kJ/mol	-1396.5 ± 3.0	-1389.7 ± 3.6
$\Delta G^\circ_{f,298}$	kJ/mol	-1289.0 ± 3.1	-1281.0 ± 3.5
V°_{298}	cm^3	42.57 ± 0.02	39.18 ± 0.01
V°_{298}	J/bar	4.257 ± 0.002	3.918 ± 0.001

of Ni_2SiO_4 are summarized in Table 5. Our value for $H^\circ_{986} - H^\circ_{298}$ for Ni_2SiO_4-olivine is somewhat larger than the values obtained by Navrotsky (1973). However, because we do not have data for Ni_2SiO_4-spinel we chose to use the results obtained by the transposed drop procedure of Navrotsky for both samples. The unweighted average value is $\Delta G^\circ_{f,298} = -1281 \pm 3.5$ kJ/mol for Ni_2SiO_4-spinel. Combining our average value for $\Delta G^\circ_{f,298}$ with our calculated entropy, we obtain $\Delta H^\circ_{f,298} = -1389.7 \pm 3.6$ kJ/mol for Ni_2SiO_4-spinel.

The Ni^{2+} ion has two unpaired spins and the spin quantum number s is 1. Therefore the entropy arising from the antiferromagnetic ordering of the spins at low temperatures is expected to be $2(R\ln 3) = 18.27$ J/(mol · K). The Néel temperature of Ni_2SiO_4-olivine, 29.15 K, is considerably lower than that of the other transition metal olivines: Fe_2SiO_4 (fayalite), 64.88 K (Robie, Finch, and Hemingway, 1982), Mn_2SiO_4 (tephroite), 47.38 K, and Co_2SiO_4-olivine, 49.85 K, (Robie, Hemingway, and Takei, 1982). Ni_2SiO_4-olivine is also less stable to decomposition into its oxide components i.e.,

$$M_2SiO_4 = 2MO + SiO_2 \; (M = Ni, Fe, Mn, Co)$$

than are the other transition metal olivines. ΔG°_{298} for this reaction being 9.55, 20.38, 21.12, and 49.42 kJ for M = Ni, Fe, Co, and Mn respectively.

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