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Thermodynamic properties of hercynite (FeAl₂O₄) based on adiabatic calorimetry at low temperatures

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ABSTRACT

The low-temperature heat capacity of hercynite (FeAl₂O₄) was measured between 3 and 400 K, and thermochemical functions were derived from the results. The measured heat-capacity curve shows a small lambda-shaped anomaly peaking at around 13 K. From our data, we suggest a standard entropy for hercynite at 298.15 K of 113.9 ± 0.2 J/(mol·K), which is some 7.6 J/(mol·K) higher than reported previously by a calorimetric study that missed the entropy contributions of the low-temperature anomaly.

INTRODUCTION

Spinels are ubiquitous minerals in the Earth's mantle and crust. Because of the additional importance of spinels as furnace smelting products, phase relations and thermodynamic properties of spinels have been investigated by numerous authors (among many others: Turnock and Eugster 1962; Buddington and Lindsley 1964; Muan et al. 1972; Bohlen et al. 1986; Nell et al. 1989; Nell and Wood 1989; Woodland and Wood 1990; Nell and Wood 1991; Sack and Ghiorso 1991). Many of these studies have focussed on thermodynamic mixing properties of spinels, aiming to understand better the behavior of complex solid solutions, which is a prerequisite for thermodynamic calculation of phase relations in complex, natural compositions.

It is surprising, however, that fundamental thermodynamic properties for many spinels of end-member composition (e.g., MgCr₂O₄, FeCr₂O₄, FeAl₂O₄, ZnCr₂O₄, ZnAl₂O₄), which should be well known before attempting to understand complex solid solutions, are only poorly understood. For example, Klemme and O'Neill (1997) and Klemme et al. (2000) investigated the standard entropy of some selected Cr- and Fe-bearing spinels. Their results, employing high-pressure high-temperature experiments and adiabatic calorimetry at low temperatures, indicated large contributions to the standard entropy probably due to magnetic ordering or phase transitions at very low temperatures (e.g., at 12.5 K in the case of MgCr₂O₄). Previous heat-capacity measurements for these phases (Shomate 1944) missed the entropy contribution from these transitions because calorimetric measurements for these phases were performed only down to temperatures of around 50 K. This is the case for many other phases of interest to geologists, as most fundamental calorimetric studies were done in the 1940s and 1950s when low-temperature equipment did not allow studies at temperatures much lower than 50 K.

There are several other phases of geological interest that undergo magnetic ordering or exhibit phase transitions at tem-

peratures lower than 50 K. One of these phases is hercynite (FeAl₂O₄). Previous heat-capacity measurements for FeAl₂O₄ extended only down to 51 K (King 1956), and the standard entropy of FeAl₂O₄ at 298.15 K ($S^0_{298.15}$) was calculated using a smooth extrapolation to 0 K without consideration of possible magnetic contributions to the entropy [S^0_{298} = 106.3 J/(mol·K); King 1956]. Although magnetic ordering phenomena were subsequently reported to occur at around 8 K (Lotgering 1962; Roth 1964), many recent thermodynamic databases (e.g., Kubaschewski and Alcock 1983; Kubaschewski et al. 1993; Barin 1995; Robie and Hemingway 1995; Binnewies and Milke 1999) accept King's (1956) value for the standard entropy for FeAl₂O₄. However, internally consistent sets of thermodynamic data (calibrated using mainly high-pressure, high-temperature experiments) indicate much higher values for the standard entropy but estimates of S^0_{298} for hercynite (FeAl₂O₄) vary substantially (Table 1).

Thermodynamic properties of FeAl₂O₄ are especially important to metamorphic geologists, as geothermobarometry of high-grade metamorphic rocks is based on several exchange equilibria involving hercynite, such as 3 FeAl₂O₄ + 3 Al₂SiO₅ = Fe₃Al₂Si₃O₁₂ + 5 Al₂O₃ or 3 FeAl₂O₄ + 5 SiO₂ = Fe₃Al₂Si₃O₁₂ + 2 Al₂SiO₅. These exchange equilibria have been investigated experimentally at high pressures and high temperatures by Hensen and Green (1971), Bohlen et al. (1986), and Shulters and Bohlen (1989). Extrapolation to more complex compositions (as to approximate natural compositions) or other temperatures and pressures than the experimental conditions requires a sound understanding of the thermodynamic properties of all involved end-member components as well as the appropriate mixing properties. For the aforementioned equilibria, thermodynamic properties of the end-members Al₂SiO₅, Al₂O₃, SiO₂, and Fe₃Al₂Si₃O₁₂ are sufficiently well understood (Robie and Hemingway 1995; see Anovitz et al. 1993 for discussion). However, those of FeAl₂O₄ are somewhat uncertain due to possible entropy contributions from magnetic ordering at low temperatures (Lotgering 1962; Roth 1964; Sack and Ghiorso 1991).

Moreover, thermodynamic phase-equilibria calculations in compositions approximating the Earth's upper mantle (e.g., the

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TABLE 1. Standard entropy of FeAl$_2$O$_4$ from the literature

	S^0_{298} [J/(mol·K)]	Type of data
King (1956)	106.3	adiabatic calorimetry
Holland & Powell (1990)	116 ± 0.8	internally consistent data
Berman (TWEEQU)	107.0	internally consistent data
Sack & Ghiorso (1991)	118.3	internally consistent data
Berman & Aranovich (1996)	123.1	internally consistent data
Gottschalk (1997)	116.9 ± 0.1	internally consistent data
Chatterjee et al. (1998)	123.2	internally consistent data
Holland & Powell (1998)	107.5	internally consistent data
Woodland, pers comm.	113.0 ± 0.8	high pressure experiments

Note: The Berman (TWEEQU) value is taken from the TWEEQU database (JUN92.GSC), but is not contained in the Berman (1991) paper.

MELTS software: cf., Ghiorso and Sack 1995; Gaetani et al. 1998) cannot be performed with much confidence if thermodynamic functions of even simple end-member spinels, such as FeAl$_2$O$_4$, FeCr$_2$O$_4$, or MgCr$_2$O$_4$, which are ubiquitous end-member components of upper mantle spinels, are not sufficiently well known.

To partially address the aforementioned matters, the present study was initiated to determine the low-temperature heat capacity of hercynite (FeAl$_2$O$_4$) between 3 and 400 K.

EXPERIMENTAL TECHNIQUES

Sample preparation and characterisation

Heat-capacity measurements were performed on synthetic polycrystalline hercynite samples. Fe$_2$O$_3$ (purity 99.99%) and Al$_2$O$_3$ (purity 99.99%) were mixed in appropriate proportions in an agate mortar under acetone. The mixture was then pressed into pellets (1.27 cm diameter) and sintered in a conventional gas-mixing vertical furnace at atmospheric pressure and 1400 °C for 24 hours using a gas mixture of CO/CO$_2$ = 75/25. The pellets were then quenched in the cold part of the furnace. Following the procedure of Harrison et al. (1998), the samples were then reground, repressed, and reannealed (using a gas mixture of CO/CO$_2$ = 85/15) at 1400 °C for 18 hours, 1100 °C for 48 hours, and 700 °C for 48 hours, before being rapidly quenched. X-ray diffraction indicated the presence of only FeAl$_2$O$_4$, as no impurities or other unreacted oxides were detected. Our synthetic hercynite had a cell parameter of a_0 = 8.1457 ± 0.0006 Å, which compares reasonably well with previous results for synthetic hercynites (Woodland and Wood 1990; Larsson et al. 1994; Harrison et al. 1998). The pellets weighed 7.97 g. Mössbauer spectra of our hercynite sample were obtained at room temperature to check for Fe^{3+}. A sample of 3.59 mg was used with a ^{57}Co source in Pd. Duplicate spectra were recorded in 512 channels of a multichannel analyzer using a velocity range of ±5 mm/s. The Mössbauer spectrum consisted of broad lines with flat tops, mainly caused by Fe^{2+}. The spectrum also indicated a weak doublet with a small quadrupole splitting and chemical shift indicative of Fe^{3+}. A fit to the spectrum yielded a Fe^{3+}/ΣFe of 0.033 (ca. 2% Fe$_3$O$_4$ component). This small Fe^{3+} content in synthetic hercynites was also observed in a number of previous studies (Rossiter 1965; Ono et al. 1966; Bohlen et al. 1986), and is apparently too small to be resolved by both X-ray diffraction and low-temperature calorimetry.

Low-temperature calorimetry

The calorimeter used, laboratory-designation CAL V, has been described before (van Miltenburg et al. 1987). More recent improvements in design and data-handling were described in van Miltenburg et al. (1998). Temperature was measured with a calibrated 27 ohm Rh/Fe thermometer (calibration by Oxford Instruments), using an automated AC bridge (Tinsley). The thermometer scale applied was the ITS-90 scale (Preston-Thomas 1990). The sample was broken into several grains of about 2 mm. A helium pressure of 1000 Pa was established to the sample chamber to promote heat exchange. Measurements were made in the intermittent mode. Stabilization periods of about 500 s were used in between the heating periods. Below 30 K, the periods were on the order of 150 s. Every temperature interval was measured at least twice, but between 4 and 30 K, the measurements were repeated four times.

Below 30 K, the reproducibility of the calorimeter is about 1%, between 30 and 100 K, 0.05–0.1%, and above 100 K, 0.03%. Checking the calorimeter with standard materials (n-heptane and synthetic sapphire) showed no deviations larger than 0.2% from the recommended values.

RESULTS AND DISCUSSION

The experimental values for the low-temperature heat capacity of hercynite are compiled in Table 2. The values have been corrected for the contribution of the empty calorimeter. The uncertainties for the heat capacities were assumed to be within 0.2%.

Figure 1 depicts the heat capacity of FeAl$_2$O$_4$ as a function of temperature. The data fit a smooth and continuous curve at temperatures above 43 K, whereas below 43 K, the data indicate a lambda transition between 4 and 43 K, peaking at around 13 K (Figs. 2 and 3). This transition was previously observed in early magnetic susceptibility measurements by Roth (1964) and is probably due to a paramagnetic to antiferromagnetic transition (Roth 1964; Sack and Ghiorso 1991).

The standard entropy at 298.15 K was calculated from the C_P data (using a T^3 extrapolation to 0 K) and resulted in $S^0_{298.15}$ = 113.9 ± 0.2 J/(mol·K). Table 2 lists our results from the C_P
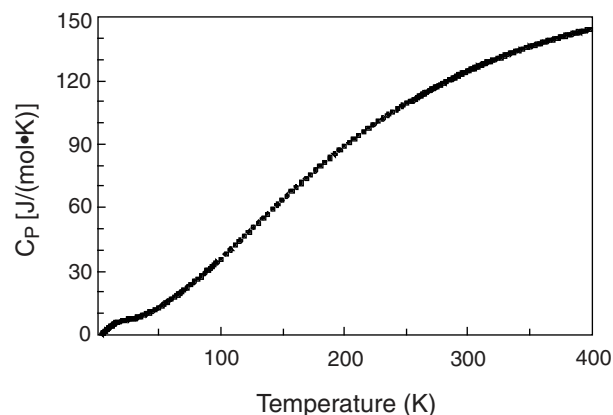

FIGURE 1. The heat capacity of polycristalline FeAl$_2$O$_4$ (hercynite) measured between 4 and 400 K. A broad heat-capacity anomaly is observed to occur between 4 and 43 K.

measurements and Table 3 compiles some selected thermodynamic properties for FeAl$_2$O$_4$. The latter were calculated from the experimental results using interpolations of the data for every degree. The interpolation procedure is such that interpolated data always pass through the experimental data. Then $S(T)$ and $H(T)$ were calculated by numerical integration. This pro-

cedure was compared to a direct integration of a fitted C_P-curve and gives the same result within the expected uncertainties.

There is no evidence of a first-order transition in hercynite (FeAl$_2$O$_4$) due to Jahn-Teller distortion of tetrahedral site Fe^{2+} with a reduction of symmetry of the crystal (Goodenough 1964). Although a first-order transition has been observed for FeCr$_2$O$_4$
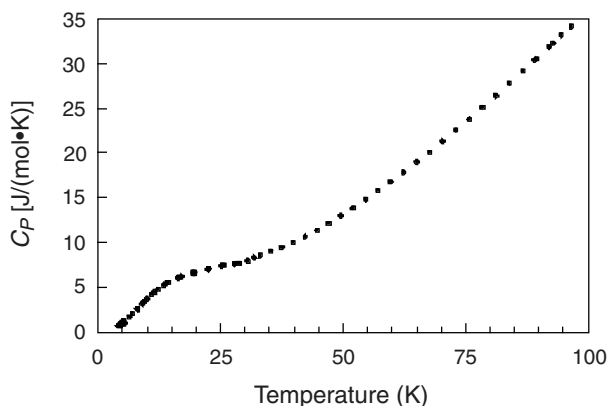

FIGURE 2. An enlarged view of the low-temperature part of the experimental data. A broad anomaly is observed between 4 and 43 K, which is probably due to a paramagnetic to antiferromagnetic transition in FeAl$_2$O$_4$ (see text for details).
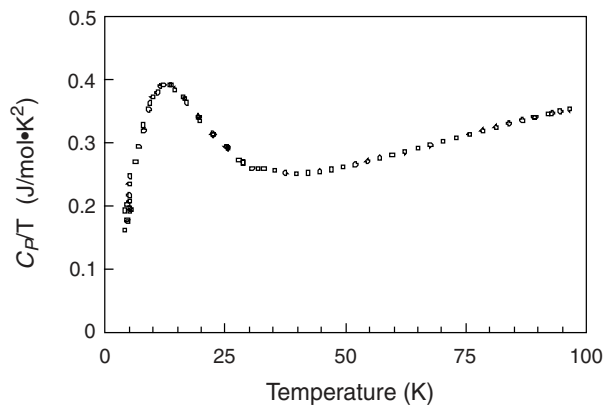

FIGURE 3. A plot of C_P/T against T. Note that the standard entropy (SDEG$_{298.15}$) is derived by integration of the C_P/T function between 0 and 298.15 K. In this plot, the anomalous behavior between 4 and 43 K is clearly visible.

TABLE 2. Experimental Molar Heat Capacities for FeAl$_2$O$_4$

T (K)	C_p [J/(mol·K)]	T (K)	C_p [J/(mol·K)]	T (K)	C_p [J/(mol·K)]	T (K)	C_p [J/(mol·K)]	T (K)	C_p [J/(mol·K)]
4.08	0.67	28.63	7.70	122.70	48.66	258.50	111.9	315.05	128.5
4.17	0.81	28.69	7.71	126.49	50.80	260.38	112.6	317.06	129.0
4.64	0.83	30.54	7.96	130.30	52.94	262.42	113.2	318.69	129.3
4.67	0.95	31.83	8.29	134.11	55.06	262.83	113.4	319.52	129.6
4.72	0.83	33.03	8.59	137.93	57.17	265.29	114.2	321.99	130.1
5.06	1.10	35.23	9.06	141.76	59.35	266.31	114.5	324.47	130.7
5.06	1.20	37.43	9.48	145.59	61.45	267.75	115.0	326.94	131.2
5.08	1.06	39.80	10.03	149.44	63.56	270.18	115.7	329.41	131.8
5.10	0.98	42.19	10.69	153.29	65.68	270.21	115.7	331.88	132.4
5.14	1.01	44.59	11.39	157.14	67.94	272.68	116.6	334.35	132.9
5.21	1.29	47.02	12.17	161.01	70.01	274.02	117.0	336.82	133.4
5.37	1.05	49.49	12.98	164.87	71.89	275.14	117.3	339.29	134.0
6.40	1.73	51.99	13.86	168.73	73.89	277.60	118.0	341.76	134.4
7.00	2.06	54.53	14.81	172.61	75.85	277.85	118.2	344.23	134.9
7.95	2.62	57.09	15.85	176.49	77.83	280.06	118.7	346.70	135.6
8.11	2.60	59.67	16.83	180.38	79.80	281.65	119.4	349.18	136.1
9.06	3.20	62.28	17.85	184.26	81.70	282.53	119.6	351.66	136.4
9.37	3.41	64.91	18.99	188.15	83.61	284.99	120.4	354.13	136.8
9.90	3.69	67.57	20.10	192.05	85.42	285.43	120.4	356.61	137.3
10.94	4.17	70.25	21.30	195.94	87.25	287.46	121.0	359.09	137.7
11.44	4.47	72.95	22.53	199.84	89.04	289.19	121.6	361.57	138.2
12.18	4.79	75.67	23.80	203.75	90.80	289.92	121.8	364.05	138.7
13.39	5.25	78.41	25.09	207.65	92.56	292.38	122.5	366.53	139.1
13.83	5.43	81.16	26.42	211.55	94.23	292.93	122.7	369.01	139.5
14.46	5.56	83.92	27.78	215.45	95.93	294.84	123.3	371.49	140.0
16.24	6.05	86.67	29.15	219.36	97.55	296.66	123.8	373.97	140.4
16.54	6.15	89.08	30.41	223.27	99.13	297.31	124.1	376.45	140.8
17.03	6.21	89.36	30.52	227.18	100.7	299.77	124.9	378.93	141.2
19.28	6.60	91.97	31.87	231.09	102.2	300.37	124.7	381.42	141.6
19.49	6.67	92.79	32.26	235.00	103.8	302.24	125.3	383.91	142.0
19.74	6.63	94.50	33.19	238.91	105.2	304.06	125.7	386.39	142.4
22.40	7.06	96.46	34.16	242.82	106.7	304.71	126.0	388.88	142.8
22.46	7.04	100.17	36.00	246.74	108.1	307.18	126.7	391.36	143.2
22.54	7.08	103.89	38.23	250.65	109.5	307.74	126.7	393.85	143.5
25.14	7.41	107.62	40.26	253.00	110.2	309.65	127.3	396.34	143.9
25.50	7.49	111.37	42.34	254.57	110.6	311.40	127.7	398.84	144.3
25.59	7.47	115.14	44.41	255.46	110.7	312.12	127.8	401.33	144.7
27.82	7.60	118.91	46.52	257.92	111.7	314.59	128.5	403.82	145.0

TABLE 3. Thermodynamic properties at selected temperatures for FeAl₂O₄

T (K)	$C^0_{P,m}$ [J/(mol·K)]	ΔS^0_m [J/(mol·K)]	ΔH^0_m (J/mol)
5	0.96	0.35	1.3
10	3.74	1.99	13.9
15	5.71	3.91	38.0
20	6.65	5.70	69.2
25	7.38	7.26	104.3
30	7.86	8.65	142.4
35	9.01	9.95	184.5
40	10.09	11.22	232.4
45	11.52	12.49	286.3
50	13.16	13.79	348.0
55	15.00	15.13	418.4
60	16.95	16.52	498.3
65	19.03	17.96	588.2
70	21.19	19.45	688.7
75	23.49	20.99	800.3
80	25.86	22.58	923.7
85	28.32	24.22	1059
90	30.84	25.90	1207
95	33.44	27.64	1367
100	35.91	29.42	1541
110	41.59	33.11	1929
120	47.13	36.97	2372
130	52.77	40.96	2872
140	58.36	45.08	3427
150	63.87	49.29	4039
160	69.49	53.60	4705
170	74.53	57.96	5425
180	79.61	62.36	6196
190	84.48	66.80	7016
200	89.11	71.25	7884
210	93.58	75.71	8798
220	97.81	80.16	9755
230	101.8	84.59	10753
240	105.6	89.01	11791
250	109.3	93.39	12865
260	112.5	97.74	13973
270	115.7	102.0	15114
280	118.7	106.3	16287
290	121.8	110.5	17490
298.15	124.4	113.9	18493
300	124.8	114.7	18723
310	127.4	118.8	19984
320	129.7	122.9	21270
330	132.0	127.0	22578
340	134.1	130.9	23908
350	136.2	134.8	25259
360	137.9	138.7	26630
370	139.7	142.5	28018
380	141.4	146.3	29423
390	143.0	150.0	30845

Note: (M = 173.8077 g).

(Shirane et al. 1964; Kose and Iida 1984), Goodenough (1964) reasoned that FeAl₂O₄ should stay cubic down to zero Kelvin, which seems to be confirmed by our data.

The total magnetic contribution to the entropy due to spin ordering of tetrahedral Fe²⁺ may be computed as R ln 5 (Gopal 1966; Sack and Ghiorso 1991), which amounts to about 119.6 J/(mol·K) when added to the lattice entropy (King 1956; this study). However, our measured value for the standard entropy of 113.9 ± 0.2 J/(mol·K) is considerably lower, indicating that the structure seems to fail to develop the full long-range magnetic order. Further work is clearly needed to further investigate the magnetic structure of hercynite at low temperatures, which may shed some light on the aforementioned descrepancy. There is considerable disagreement among internally consistent estimates for the standard entropy of FeAl₂O₄ (cf., Table 1), and our data are close to the lower end of these estimates.

Although we have further constrained the standard entropy of FeAl₂O₄ using low-temperature calorimetry, thermodynamics of FeAl₂O₄ are not yet fully understood, as there are neither high-temperature heat-capacity data nor high-temperature heat-content data published in the literature. Therefore, only estimated high-temperature heat-capacity functions are available (e.g., Robie and Hemingway 1995; Sack and Ghiorso 1991), which bear considerable uncertainties. The determination of the high-temperature heat capacity of FeAl₂O₄ remains an important task for experimentalists.

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