

## Thermodynamics of Fe(II)Fe(III) oxide systems

### I. Hydrothermal Fe<sub>3</sub>O<sub>4</sub><sup>a</sup>

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The heat capacity of a hydrothermally-prepared polycrystalline sample of Fe<sub>3</sub>O<sub>4</sub> was measured from 53 to 350 K, primarily to study the thermophysics of the Verwey transitions. Although the bifurcation of the transition was confirmed, the sample was found to contain traces of manganese. The observed transition temperatures of 117.0 and 123.0 K are 3.7 and 4.2 K higher respectively than those found in pure Fe<sub>3</sub>O<sub>4</sub>. Ancillary analytical results are consistent and indicate a stoichiometry of Mn<sub>0.008</sub>Fe<sub>2.992</sub>O<sub>4</sub> for this material. Characteristics in the transition region are ascribed to dopant effects.

### Introduction

To verify the reality of the bifurcated heat-capacity anomaly found by Westrum and Grønvd<sup>(1)</sup> on a synthetic polycrystalline Fe<sub>3</sub>O<sub>4</sub> sample (subsequently characterized as having unusually high purity<sup>(2)</sup>) heat-capacity measurements were made on a hydrothermally prepared Fe<sub>3</sub>O<sub>4</sub> sample. Although the sample, originally reported to be very pure, did indeed confirm the reality of the bifurcation, unexpected contamination (primarily by manganese) gave a resultant composition: (Mn<sub>0.008</sub><sup>2+</sup>Fe<sup>3+</sup>) [Fe<sub>0.992</sub><sup>2+</sup>Fe<sup>3+</sup>]O<sub>4</sub> (in the usual symbolism of indicating tetrahedral and octahedral sites of the inverse-spinel structure with ( ) and [ ], respectively) and the then surprising result that the transition peaks were displaced to higher temperatures. The consideration and presentation of these results<sup>(3,4)</sup> encouraged the development of a systematic program to learn the effect of selected tetrahedral- and octahedral-site dopants in Fe<sub>3</sub>O<sub>4</sub> on the temperatures and magnitudes of the excess heat capacity

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in the insulator-to-conductor transition to elucidate the nature of the Verwey transition.<sup>(1)</sup>

Adiabatic calorimetry has proved to be a highly successful technique in this initial application to the study of phenomena associated with metal-to-non-metal electronic transitions even although partly occasioned by (inadvertent) dopants. The high precision, ease of temperature control, and—perhaps most of all—determination under equilibrium conditions have proved both convenient and essential.

#### SYNTHESIS OF SAMPLE

A charge consisting of a 71.96 g iron in pellet form (National Bureau of Standards Standard Sample 55e), 303.79 g of reagent  $\text{Fe}_2\text{O}_3$  (Fisher Scientific Co. Lot 780323), and  $300\text{ cm}^3$  of  $1\text{ mol kg}^{-1}$   $\text{NH}_4\text{Cl}$  solution were reacted in a  $1.1\text{ dm}^3$  platinum-lined pressure vessel under mechanical oscillation at 573 K for 3 d. The product was removed from the vessel and washed with copious amounts of distilled demineralized water in a Buchner funnel. Aspiration was used to draw off the  $\text{NH}_4\text{Cl}$  solution and wash water quickly and reduce the potential for oxidation of the product. The crystalline product was vacuum dried at 300 K for 36 h and sealed in silica tubes for transport. The yield was 376.8 g or 95.8 per cent of theoretical. The losses were due to (1) small amounts of iron(II) in solution, (2) product lost in the pressure fittings, and (3) product lost in transfers and washings.

$\text{NH}_4\text{Cl}$  solution was chosen over other chlorides, including HCl, as the reacting solution because the solution is acidic at 573 K and nearly neutral at 300 K. Hence, although significant aqueous iron(II) concentration exists at the reaction temperature, a much lower concentration occurs at 300 K. The latter insures that little or no surface film of hydrated iron oxides was formed by air oxidation of the dissolved ions during washings.

#### SAMPLE CHARACTERIZATION

Atomic emission spectroscopy and wet chemical analysis showed 0.2 mass per cent Mn, 0.02 mass per cent Ni, and less than 0.02 mass per cent for the sum of all other impurities. Interpretation of X-ray powder diffraction results<sup>(2)</sup> and knowledge of the site preference of Mn indicate the chemical formula to be:  $(\text{Mn}_{0.008}^{2+}\text{Fe}^{3+})[\text{Fe}_{0.992}^{2+}\text{Fe}^{3+}]\text{O}_4$ .

Magneto-t.g.a. determinations indicated a Néel temperature of 863 K, taken as the maximum change in slope of the curve of magnetization against temperature. The magnetic disordering occurred over the temperature range 825 to 886 K. This compares with the Néel temperature of 868 K and 856 to 888 K range for pure  $\text{Fe}_3\text{O}_4$ .

#### CALORIMETRIC TECHNIQUE

Heat-capacity measurements were made in the Mark III adiabatic cryostat over the range 65 to 350 K. Details of the cryostat construction and measuring circuit calibration have been described.<sup>(5)</sup> A sample mass of 212.4474 g was loaded into the gold-plated calorimeter W-42 which has an internal volume of  $93.0\text{ cm}^3$ . After evacuation, the calorimeter was back-filled with a pressure 70.0 Torr of helium gas

to aid thermal contact and equilibration between calorimeter, sample, and the heater + thermometer assembly.† Temperatures were measured with a capsule-type platinum resistance thermometer (A-3) calibrated by the National Bureau of Standards. Calibration is referred to the IPTS-48, Text Revision of 1960<sup>(6)</sup> defined between 90.18 K and 903.65 K. The National Bureau of Standards 1955 provisional scale was employed at lower temperatures; 273.15 K was used as the melting point of ice.

### Results and discussion

Experimentally observed molar heat capacities are listed in table 1 in chronological sequence so that the temperature increments used in the measurements can usually be deduced from the adjacent mean temperatures. Based upon the chemical formula cited, a molar mass of  $231.539 \text{ g mol}^{-1}$  was used. The heat capacity is compared with that of pure  $\text{Fe}_3\text{O}_4$  in figure 1.

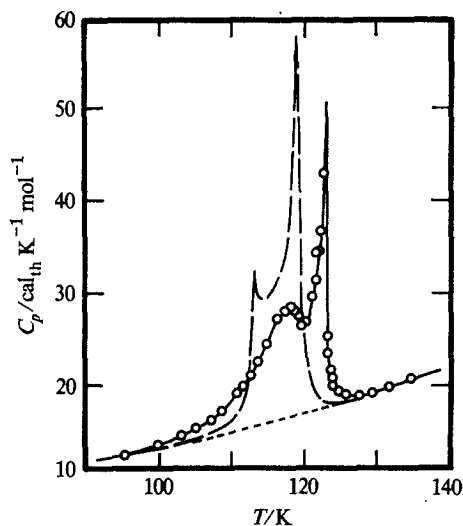


FIGURE 1. Comparison of the heat capacities of pure  $\text{Fe}_3\text{O}_4$ :<sup>(3)</sup> - - - - -; and of hydrothermal magnetite  $\text{Mn}_{0.008}\text{Fe}_{2.992}\text{O}_4$ : —○—.

Values of the smoothed heat capacities at selected temperatures are given in table 2 together with the derived thermodynamic functions integrated by digital computer. The accuracy of the individual determinations of heat capacity on this sample are probably somewhat less than is usual for such results from this laboratory based on the purity of the sample, calibration of the apparatus and circuits, interlaboratory comparisons on the heat capacity of Calorimetry Conference samples of benzoic acid and synthetic sapphire, because of problems in the measurement of the heat

† Throughout this paper Torr = (101.325/760) kPa, atm = 101.325 kPa, and cal<sub>th</sub> = 4.184 J.

TABLE 1. Experimental heat capacity of hydrothermal  $\text{Fe}_3\text{O}_4$   
 ( $\text{cal}_{\text{th}} = 4.184 \text{ J}$ )

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Series II		Series V		196.49	27.56	121.31	27.53
84.39	9.94	101.34		209.75	28.94	121.99	31.62
94.84	12.19	Enthalpy Detn. A		222.49	30.21	122.59	35.34
100.27	13.47			234.77	31.34	123.17	34.99
101.60	13.91	Series VI		248.69	32.21	123.91	21.06
103.30	14.55	65.532	6.306	258.32	33.23	119.82	27.85
105.35	15.29	80.453	9.137	265.97	33.89	122.37	32.50
107.31	16.24	91.704	11.497	269.04	34.05	122.92	40.58
108.80	17.16	Enthalpy Detn. B		270.47	33.97	123.56	23.55
109.88	17.85	123.65	23.51	271.05	32.92	124.42	19.70
110.90	18.98	129.59	19.27	271.81	34.31	125.35	19.09
111.89	19.85	135.92	20.08	273.03	34.31		
112.83	21.01	144.62	21.25	274.49	34.51	Series XVI	
113.73	22.55	150.43	22.04			53.37	4.164
114.57	23.99	156.07	22.71	Series XII		56.99	4.764
115.37	25.18	160.47	23.33	241.89	31.88	60.20	5.329
116.14	26.38	168.44	24.34	250.28	32.58	63.11	5.855
116.87	27.31	176.13	25.25	258.62	33.19	66.61	6.489
117.59	28.14			266.92	34.13	71.94	7.465
118.30	28.51	Series VII		272.18	33.30	77.98	8.640
119.25	27.63	93.03	11.786	274.44	34.38	83.33	9.727
		108.93	19.32	276.66	34.61	88.19	10.768
Series III		121.90	26.52	281.87	34.96	92.67	11.668
117.06	23.87	122.02	28.89	290.02	35.51	97.34	12.717
118.12	28.08	122.14	30.68	298.05	36.10	102.13	14.106
118.73	27.43	122.25	32.45			106.51	15.92
119.22	27.77	122.35	32.56	Series XIII		110.42	18.59
119.72	27.04	122.45	33.86	84.23	9.910	113.78	22.86
120.36	27.11	122.55	36.53	90.29	11.201	116.63	27.20
121.10	27.99	122.65	32.60	96.64	12.580	119.23	27.76
		122.75	35.86	105.11	15.329	121.49	29.60
		122.85	38.09	112.01	20.41	122.57	31.46
Series IV		122.94	39.93	117.38	27.57	122.76	34.53
104.11	14.91	123.03	43.27			122.93	40.04
111.33	19.72	123.11	39.75	Series XIV		123.09	46.78
115.19	24.48	123.19	42.62	(Non-equilibrium quench-cooled)		123.28	28.09
116.48	27.31	123.31	25.29	121.30	29.41	123.53	23.28
117.70	28.08	123.44	23.42	122.69	32.77	123.81	20.98
118.53	28.51			122.93	40.30	124.11	19.98
119.00	28.07	Series X		123.14	42.16	124.42	19.49
119.49	27.24	173.39	25.05	123.41	24.87	126.31	19.01
119.99	26.70	179.00	25.61	123.37	21.38	129.75	19.13
120.48	26.92	185.73	26.37	123.75	21.72	134.49	19.80
120.98	27.35	192.93	27.29	124.15	20.15	140.40	20.65
121.45	29.80	199.94	27.93			146.11	21.46
121.89	31.24	206.79	28.61	Series XV		151.64	22.19
122.31	34.52	213.51	29.25	69.57	7.026	157.01	22.91
122.70	36.72	220.08	29.94	77.57	8.554	164.13	23.81
123.05	43.07			87.87	10.681	171.90	24.78
123.64	22.68	Series XI		107.74	18.61	179.41	25.67
124.56	19.58	184.55	26.10			186.71	26.50
125.54	19.09					194.53	27.37

TABLE 1—continued

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Series XVI (cont.)		252.35	32.75	176.96	34.61	Series XVII	
201.47	28.09	258.27	33.30	282.64	35.01	299.35	36.16
208.25	28.80	264.11	33.80	288.27	35.42	313.51	37.14
214.89	29.42	267.76	34.37	293.83	36.05	320.04	37.45
221.40	30.05	269.24	33.75	299.34	35.79	326.51	37.80
227.79	30.62	270.70	34.08	304.84	36.46	332.90	38.43
234.10	31.53	271.89	34.52	310.76	36.88	339.26	38.27
240.25	31.73	272.77	34.40	317.11	37.24	345.58	28.94
246.34	32.22	273.66	34.17				

capacity of the empty calorimeter. Hence standard deviations of the smoothed heat-capacity values are 0.08 per cent above 30 K; those in the derived functions about 0.06 per cent. A terse summary of the thermodynamic functions is given in table 2, details at selected temperatures at 10 K intervals over the range of measurement are given elsewhere.<sup>(7)</sup> The thermodynamics of the Verwey transition are summarized in table 3.

TABLE 2. Thermodynamic functions for hydrothermal Fe<sub>3</sub>O<sub>4</sub>  
(cal<sub>th</sub> = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{S^\circ(T) - S^\circ(60 \text{ K})\}}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{H^\circ(T) - H^\circ(60 \text{ K})\}/T}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
60	5.275	0	0
100	13.520	4.495	3.6552
200	27.96	20.04	13.303
300	36.18	33.06	19.663
350	39.07	38.87	22.239
273.15	34.32	29.76	18.129
298.15	36.06	32.84	19.561

TABLE 3. Enthalpy and entropy of the Verwey transition for hydrothermal Fe<sub>3</sub>O<sub>4</sub>  
(cal<sub>th</sub> = 4.184 J)

Enthalpy Detn.	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{H(T_2) - H(T_1)}{\text{cal}_{\text{th}} \text{mol}^{-1}}$	$\frac{H(134 \text{ K}) - H(96 \text{ K})}{\text{cal}_{\text{th}} \text{mol}^{-1}}$
Series V	105.63	133.51	616.67	756.28
Series VI	96.71	127.01	615.00	759.59

Mean value: 757.9  
-Lattice: 619

Enthalpy of transition:  $\Delta H_t/\text{cal}_{\text{th}} \text{mol}^{-1} = (139 \pm 1)$   
Entropy of transition:  $\Delta S_t/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1} = (1.18 \pm 0.01)$

Variation in the heat capacities in the transition region was observed with changes in the cooling rates. Figure 2 depicts the effect of differing cooling rates upon the lower-temperature side of the higher-temperature transition. These results were obtained by cooling at differing rates through the heat-capacity maximum in the high-temperature transition, the value of which was invariant, stopping the cooling

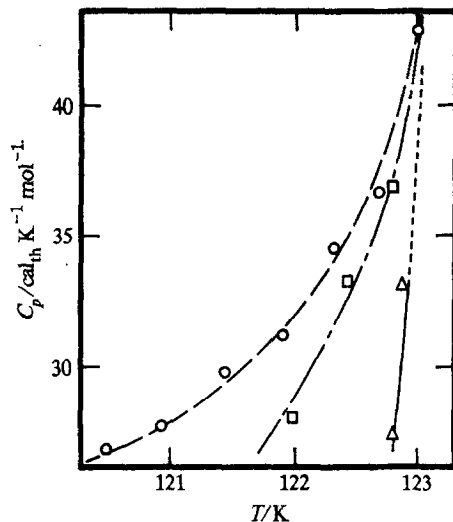


FIGURE 2. The effect of cooling rate and extent of cooling upon  $T_2$  of hyd- $\text{Fe}_3\text{O}_4$ . The several curves represent: —○—○—, cooled through the transition to 50 K over 96 h; —□—□—, cooled just through the  $T_2$  peak at  $0.1 \text{ K h}^{-1}$ , and —△—△—, cooled just through the  $T_2$  peak at  $14 \text{ K h}^{-1}$ .

after reaching about 120 K, and making a series of heat-capacity measurements. However, cooling to 90 K or lower and maintaining the calorimeter at or below that temperature for at least 4 h always permitted reproduction of the transitional "envelope".

The six experimental series through the transition region yielded about 80 heat-capacity points consistent with a smooth curve to about  $\pm 0.02$  per cent. Compared with resistivity and magnetic measurements in which thermocouples are employed as the temperature standard, adiabatic calorimetric techniques are about ten times greater in sensitivity. This study demonstrates that achievement of equilibrium—even in cooling through the transition—is a necessary criterion for evaluation of the transitional behavior of  $\text{Fe}_3\text{O}_4$ .

After a typical energy input to the sample in the transition region produced a temperature increment of 0.5 to 3.0 K, 0.7 to 1.5 h was required to achieve thermal equilibration. The longer equilibrium times were associated with the larger  $\Delta T$ 's. This behavior suggests that the mechanism of the higher-temperature transition is kinetically faster than that of the lower. Further implications are discussed elsewhere.<sup>(2, 3)</sup>

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