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Heat capacities of Fe_3O_4 and $ZnFe_2O_4$ from 300 to 500 K

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Heat-capacity determinations were made on $ZnFe_2O_4$ and Fe_3O_4 to extend cryogenic data on $ZnFe_2O_4$,[1] and Fe_3O_4.[2] These materials have been investigated at these higher temperatures to seek a correlation between the heat capacity and changes in the trend of the resistivity of Fe_3O_4 near 350 K observed by Domencali.[3] Since no obvious C_p anomaly was detected in Fe_3O_4, $ZnFe_2O_4$ was also examined by adiabatic calorimetry to model the harmonic lattice for Fe_3O_4.

Both samples were those used in previous investigations.[1, 2] Measurements were made in the Mark IV adiabatic thermostat.[4] Calorimeter loading information is listed in table 1; experimental molar heat capacities are given in table 2. Thermodynamic functions (listed in table 3) were computer-generated from a least-squares

TABLE 1. Calorimeter loading information: sample mass m, molar mass M, and He pressure p

(Torr = (101.325/760) kPa)

Compound	$\frac{m}{\text{g}}$	$\frac{M}{\text{g mol}^{-1}}$	Calorimeter	$\frac{p}{\text{Torr}}$
Fe_3O_4	124.101	231.539	W-22-P (83.76 cm^3)	29.5
$ZnFe_2O_4$	175.996	241.080	W-22-R (84.31 cm^3)	98.0

fit of the experimental heat capacities combined with similar values above 120 K from the earlier cryogenic data measured from 5 to 350 K. The function $\{G^\circ(T)-H^\circ(0)\}/T$ has not been tabulated since the existence of zero temperature entropy in the spinel structure has not been resolved.

Figure 1 reveals the absence even of a subtle anomaly in the C_p of Fe_3O_4 referred to that of $ZnFe_2O_4$ over the investigated temperature region, for the difference between their heat capacities is maintained throughout. The anomalously high C_p of Fe_3O_4 relative to that of other ferrospinels will be discussed in subsequent papers.

TABLE 2. Experimental heat capacities of $ZnFe_2O_4$ and Fe_3O_4 ($cal_{th} = 4.184$ J)

T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$
			$ZnFe_2O_4$—Mark IV				
Series I		366.56	36.36	448.15	38.49	532.00	39.90
302.65	33.73	376.96	36.70	458.73	38.74	542.32	40.14
312.92	34.24	387.28	37.00	469.25	38.93		
323.05	34.74	397.53	37.31	479.82	39.15	Series II	
333.06	35.36	407.69	37.57	490.36	39.35	444.31	38.66
339.24	35.38	417.79	37.84	500.83	39.56	454.60	38.66
348.15	35.70	427.83	38.04	511.26	39.77	464.88	38.91
356.96	35.99	437.80	38.29	521.67	39.83	475.10	39.06
			Fe_3O_4—Mark IV				
Series I		Series II		444.54	43.54	538.76	47.06
304.50	36.57	353.25	39.47	453.59	43.95	547.92	47.41
316.45	37.32	366.01	40.12	462.58	44.28		
328.20	38.02	378.63	40.79	471.52	44.66		
339.77	38.70	388.22	41.24	480.39	44.99	Series III	
351.17	39.37	397.72	41.65	489.20	45.30	478.25	44.76
362.42	39.98	407.14	41.98	497.96	45.61	488.57	45.13
373.50	40.59	416.47	42.48	510.89	45.94	498.81	45.51
384.45	41.08	425.74	42.83	520.25	46.28	508.96	45.81
		435.41	43.22	529.54	46.72	519.04	46.21

TABLE 3. High-temperature thermal functions of $ZnFe_2O_4$ and Fe_3O_4 ($cal_{th} = 4.184$ J)

T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	$\{S°(T) - S°(0)\}$/$cal_{th}\,K^{-1}\,mol^{-1}$	$\{H°(T) - H°(0)\}/T$/$cal_{th}\,K^{-1}\,mol^{-1}$
	$ZnFe_2O_4$		
300	33.22	36.22	18.108
400	37.36	46.42	22.474
500	39.52	54.78	25.604
550	40.25	58.82	26.977
	Fe_3O_4		
300	36.18	35.14	19.945
400	41.75	46.36	24.744
500	45.59	56.11	28.549
550	47.51	60.54	30.181

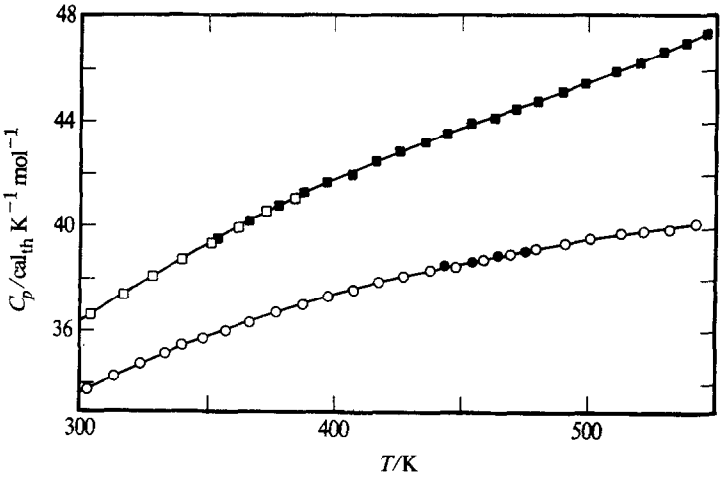

FIGURE 1. Heat capacities of Fe_3O_4 (Series I = □; Series II = ■; Series III omitted to avoid confusion); $ZnFe_2O_4$ (Series I = ○; Series II = ●).

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