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LOW TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ZINC FERRITE*

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Abstract—The heat capacity of zinc ferrite ($ZnFe_2O_4$) has been determined over the range 5 to 350°K. Molal values of C_p,S^0, and $H^0-H_0{}^0$ computed from the thermal data are $32{\cdot}99\pm0{\cdot}03$ cal/deg., $36{\cdot}01\pm0{\cdot}03$ cal/deg., and $18{\cdot}00\pm0{\cdot}02$ cal, respectively, at 298·15°K. A co-operative thermal anomaly associated with antiferromagnetic ordering occurs at 9·5° and extends toward higher temperatures probably as a consequence of persisting short range order.

INTRODUCTION

ZINC ferrite, $ZnFe_2O_4$, crystallizes in the normal spinel structure. A well-tempered zinc ferrite is, therefore, characterized by having the iron atoms located at the centers of octahedra of oxygen atoms and the zinc atoms centered in tetrahedra of oxygen atoms. Conversely, an inverted spinel contains the divalent cation on octahedral sites; since there are twice as many octrahedral sites as tetrahedral sites in the spinel structure, half of the trivalent iron atoms also occupy octrahedral sites. Typically, the inverted spinels are ferrimagnetic and the normal spinels are paramagnetic at room temperature. Since the exchange interactions between cations on octahedral sites are antiferromagnetic in nature, some type of antiferromagnetic ordering may take place in zinc ferrite at low temperatures.

Although the fairly complex magnetic properties of ferrospinels have been extensively investigated by various techniques, few of these measurements have extended below 10°K. Utilization of low temperature adiabatic calorimetry permits both the detection of magnetic transformations and the evaluation of the thermodynamic parameters associated with these phenomena. This calorimetric technique is relatively sensitive, precise and, compared to more direct magnetic measurements (e.g., susceptibility), less subject to being masked by traces of ferromagnetic impurities.

The study of the low temperature thermal properties of a series of nickel-zinc ferrites⁽¹⁾ of empirical formula $Ni_{1-x}Zn_xFe_2O_4$ over the range $x = 0{\cdot}6$ to $x = 0{\cdot}9$ revealed an anomalously high heat capacity in the vicinity of 9°K, the magnitude of which increases rapidly as x approaches unity. Recent measurements by FRIEDBERG *et al.*⁽²⁾ on a sample approximating zinc ferrite in composition confirmed the obvious extrapolation to $x = 1$ in revealing the existence of an anomalous peak in the heat capacity of zinc ferrite ($ZnFe_2O_4$) with a maximum near 9°K and a prominent "tail" on the high temperature side. Low temperature neutron diffraction studies by HASTINGS and CORLISS⁽³⁾ have demonstrated the existence of this transition and strongly suggest that it results from an antiferromagnetic ordering.

However, the thermal anomaly reported by FRIEDBERG⁽⁴⁾ in zinc ferrite is considerably rounded and broadened compared to other co-operative transformations and reveals no evidence of a discontinuity in the derivative of the heat capacity with respect to temperature. Such deviation from the usual behavior of co-operative transitions might be expected as a consequence of partial inversion of the "normal" spinel structure, of inhomogeneity on an atomic scale, or of deviation from exact

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stoichiometry in the sample utilized in these measurements. Further investigation of the thermal properties of this substance was, therefore, considered relevant to the understanding of the ordering phenomenon.

EXPERIMENTAL

Preparation of the zinc ferrite

Preliminary investigation revealed the strong dependence on composition of the heat capacity of nickel-zinc ferrites in the vicinity of 10°K. For reasons already indicated,⁽¹⁾ great care was exercised in the preparative technique to obtain, as nearly as possible, a stoichiometric, homogeneous, non-inverted sample of zinc ferrite.

Equimolal quantities of weighed, anhydrous, chemically pure ZnO and Fe_2O_3 were milled in a hardened-steel ball mill using a thin acetone slurry. After passing the slurry through a magnetic separator, the bulk of the acetone was decanted and the remainder evaporated. Cylindrical slugs of about 50 g mass were pressed; the surface layer was removed, and the slugs were fired in air at 1100°C for 14 hr. After furnace cooling, the slugs were sufficiently fragmented in a hardened-steel "diamond mortar" to pass a 30 mesh screen. These granules were reformed into slugs, fired at 1100°C for 12 hr, and gradually allowed to cool in the furnace to 30°C over a period of 16 hr. The resulting ferrite granules were of a uniform reddish-brown color throughout.

Gravimetric chemical determinations showed 46·24 ± 0·1 per cent iron (theoretical: 46·33) and 27·2 ± 0·1 per cent zinc (theoretical: 27·12). Spectro-chemical analyses revealed 0·01 to 0·1 per cent of Al and Mn and 0·001 to 0·01 per cent of Ca, Cu, Mg, Ni, and Si. Stannous chloride redox titration indicates less than 0·1 per cent ferrous iron in the samples.

Cryogenic technique

The Mark I adiabatic cryostat used for these measurements has been described.(5) Measurements were made in a calorimeter (Laboratory Designation W-9) which is similar in design and dimensions to W-6(6) except for the following modifications: only four conduction vanes were used, protection against possible corrosion was achieved by a 0·02 mm gold plate on the interior surfaces, and a weighed quantity of Apiezon T vacuum grease was used to provide thermal conduction in the thermocouple sleeve and in the thermometer-heater well. The calorimeter contained 2·0 cm helium pressure to improve thermal conduction in the sample space. Temperatures were measured with a capsule-type platinum resistance thermometer (Laboratory Designation A-3) inserted within the heater sleeve in the wall. A 150 Ω glass-fibre-insulated, constantan wire was bifilarly wound in a double-thread groove in the heater sleeve. The thermometer was calibrated by the National Bureau of Standards against the International Temperature Scale above 90°K and by comparison at 19 temperatures with the Bureau's platinum thermometers(7) over the range 10–90°K.

Below 10°K we established a provisional temperature scale by fitting the constants in the equation(8) $R = A+BT^2+CT^5$ to the observed resistance of the thermometer at 10°K, the resistance at the boiling point of helium, and dR/dT at 10°K. The temperature scale thus defined probably agrees with the thermodynamic scale to 0·1° below 10°K, 0·03° from 10 to 90°K, and 0·05° from 90 to 400°K.

Measurements of temperature and of electrical energy

Table 1. Molal heat capacity of zinc ferrite

(in cal/deg⁻¹ g/mole⁻¹)

T(°K)	C_p
Series I	
184·44	24·00
193·52	25·00
203·27	25·99
212·90	26·93
222·68	27·80
232·53	28·65
242·39	29·43
252·28	30·16
262·21	30·85
272·28	31·44
282·53	32·10
292·86	32·71
303·14	33·25
313·31	33·77
323·41	34·23
333·65	34·66
343·93	35·11
Series II	
7·81	2·6
8·47	3·9
8·87	5·9
9·18	7·9
9·41	9·2
9·76	6·5
10·18	4·17
10·91	3·37
Series III	
5·50	0·58
6·24	1·11
6·82	1·50
7·48	2·08
8·46	3·28
8·89	5·3
9·39	(8·7)
9·75	(8·3)
10·38	3·86
11·10	3·272
Series III (cont.)	
11·82	3·034
12·95	2·787
13·66	2·635
14·70	2·457
15·85	2·271
16·97	2·127
18·31	1·989
20·14	1·848
22·28	1·755
24·45	1·723
26·74	1·749
29·39	1·848
32·55	2·045
36·01	2·341
39·61	2·716
43·47	3·176
47·72	3·740
52·45	4·413
Series IV	
17·04	2·123
18·69	1·957
52·37	4·298
58·05	5·246
64·00	6·173
69·98	7·115
76·16	8·097
82·61	9·183
89·79	10·335
97·61	11·608
105·53	12·900
111·99	13·917
120·25	15·232
128·58	16·526
137·08	17·81
146·07	19·11
155·56	20·42
165·25	21·70
175·00	22·90
184·94	24·06

were made with an autocalibrated White double potentiometer. A timer operated by an electrically driven 240-cycle tuning fork and amplifier automatically indicated the duration of the energy input. Three independent determinations of the heat capacity of the empty calorimeter have been made over the entire temperature range.

RESULTS

The experimental values of the observed molal heat capacity of zinc ferrite are presented in Table 1. These data include small corrections for the slight differences in the amounts of helium and solder between the full and the empty calorimeter and for the finite temperature increments used in the measurements. Since the data are listed in chronological sequence, the temperature increments of the individual determinations can be estimated from the adjacent mean temperatures.

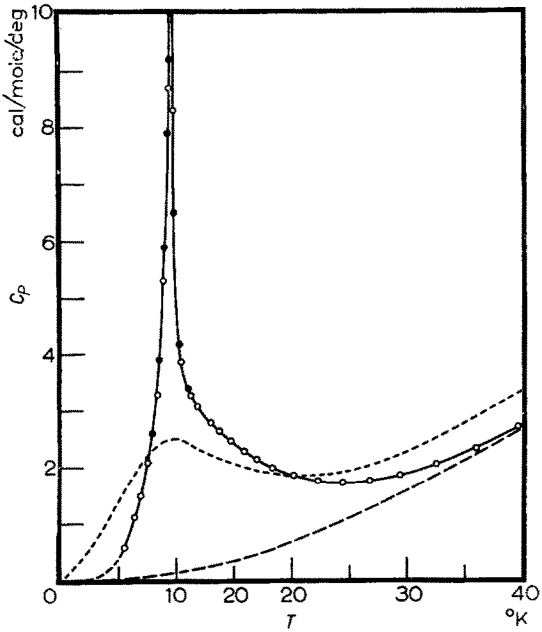

FIG. 1. The molal heat capacity of zinc ferrite from 5 to 40°K. The dotted curve represents the measurements of FRIEDBERG *et al.*(2) and the dashed curve approximates the lattice (vibrational) heat capacity.

The data are expressed in terms of the defined thermochemical calorie equal to 4·1840 absolute joules. The ice point is taken as 273·15°K, and the gram formula weight of $ZnFe_2O_4$ as 241·08. A sample of 163·397 g was employed. Fig. 1 depicts the heat capacity in the vicinity of the observed thermal anomaly.

The molal heat capacity and thermodynamic functions derived by numerical integrations of the heat capacity are listed at rounded temperatures in Table 2. The heat capacity values were read from a smooth curve through the experimental points and are estimated to have a probable error of 0·1 per cent down to 25°K increasing to 1 per cent at 10°K. The probable error may be 10 per cent below 10°K as a consequence of the sharp dependence of heat capacity on temperature over the region of thermal anomaly and the relatively slow establishment of thermal equilibrium in this region. The deviation of the individual experimental determinations from our smoothed curve are presented in Fig. 2. Solid lines represent deviations of ±0·1 per cent and ±1·0 per cent, respectively. Below 5°K, a Debye third power extrapolation was used to obtain values of the thermodynamic functions. The probable

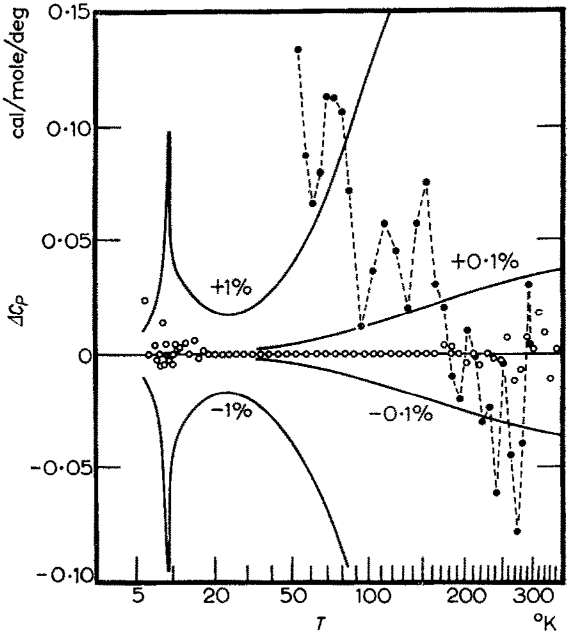

FIG. 2. The deviation of the measured heat capacities of zinc ferrite from smooth curve, i.e.,

$$\Delta C_p = C_{p(\text{experimental determination})} - C_{p(\text{curve})}$$

The open circles represent the individual experimental determinations of this work. The solid circles are those reported by KING.(9)

Table 2. Molal thermodynamic functions of zinc ferrite

T(°K)	C_p (cal/deg.)	S^0 (cal/deg.)	$(H^0 - H_0{}^0)$ (cal)	$-\frac{(F^0 - H_0{}^0)}{T}$ (cal/deg.)
10	4·68	2·2126	17·69	0·4431
15	2·400	3·4473	32·65	1·2705
20	1·857	4·0520	43·11	1·8966
25	1·724	4·4459	51·92	2·3692
30	1·878	4·7701	60·82	2·7427
35	2·248	5·0852	71·07	3·0548
40	2·758	5·4173	83·53	3·3291
45	3·376	5·7766	98·82	3·5807
50	4·059	6·1673	117·38	3·8197
60	5·552	7·0370	165·29	4·2821
70	7·117	8·0095	228·58	4·7441
80	8·721	9·0639	307·7	5·2173
90	10·368	10·1863	403·2	5·7067
100	12·004	11·363	515·0	6·213
110	13·598	12·583	643·1	6·737
120	15·196	13·835	787·1	7·276
130	16·738	15·112	946·8	7·829
140	18·236	16·408	1121·7	8·396
150	19·658	17·715	1311·2	8·973
160	21·01	19·027	1514·5	9·561
170	22·29	20·339	1731·1	10·156
180	23·48	21·648	1960·0	10·759
190	24·62	22·949	2200·6	11·367
200	25·67	24·239	2452·1	11·979
210	26·65	25·515	2713·7	12·592
220	27·56	26·776	2984·8	13·208
230	28·43	28·020	3264·8	13·825
240	29·25	29·247	3553·3	14·442
250	30·00	30·458	3849·6	15·059
260	30·70	31·647	4153·1	15·673
270	31·34	32·818	4463·4	16·287
280	31·96	33·970	4779·9	16·899
290	32·54	35·102	5102·4	17·507
300	33·08	36·214	5430·5	18·112
350	35·35	41·493	7143·8	21·082
273·15	31·54	33·184	4562·7	16·481
298·15	32·99	36·010	5369·8	18·000

errors in the entropy, enthalpy, and free energy function are estimated to be 0·1 per cent above 100°K, but for internal consistency one more digit has been retained than is justified by the estimated probable error. The effect of nuclear spin and isotope mixing is not included in the entropy and the free energy function.

DISCUSSION

After the completion of these measurements, heat capacity data on zinc ferrite from 51 to 298°K were reported by KING.(9) The deviations of KING's data from our smoothed curve are shown in Fig. 2. The data of KING trend gradually to higher values toward lower temperatures than do the results of the present research; however, the agreement is good at room temperature. By virtue of compensation of these deviations of opposite sign, the entropy increments ($S_{298\cdot16°K}-S_{51°K}$) are in close agreement. Below 51°K, the extrapolated portion of KING's entropy is in error by nearly four units. This emphasizes the desirability of extending heat capacity measurements to the lowest practicable temperatures when such data are intended for evaluation of chemical thermodynamic functions. Isolated experimental points obtained by FRIEDBERG *et al.*(2) over the range 80 to 200°K appear to be at least 5 per cent higher than those reported either in the present work or by KING.

The existence of a typical co-operative type heat capacity anomaly rising to a sharp maximum greater than 9 cal/mole/deg. at 9·5±0·2°K accompanied by a prominent "tail" possibly extending beyond 25°K is characteristic of pure zinc ferrite. However, because thermal equilibrium was so slowly achieved below 10°K, it was desirable to traverse this entire anomaly with a single energy input and then to compare the directly measured enthalpy with that obtained by the integration of the C_p curve (Fig. 1) over the corresponding range. The results of three such tests are summarized in Table 3 and indicate good accord with the heat capacity measured with small temperature increments.

The anomaly as reported by FRIEDBERG *et al.*,(2) is indicated by the dotted line in Fig. 1. The observed difference is probably due to deviations from exact stoichiometry, from inhomogeneity, and/or from partial inversion suggested by the mode of preparation and the reported properties of their sample.(2,4) That the thermal history of the ferrite specimen may have a marked effect on heat capacity over a wide temperature range has recently been demonstrated for lithium-zinc ferrite.(10)

Table 3. Comparison of measured and integrated enthalpy increments

T_{initial}(°K)	T_{final}(°K)	$\Delta H_{\text{measured}}$	$\Delta H_{\text{integrated}}$
5·16	25·23	52·7	51·7
5·03	14·12	31·6	30·0
5·03	16·07	36·7	36·1

Although it is not yet possible satisfactorily to resolve the magnetic and lattice contributions to the specific heat, a rough approximation may be obtained by fitting the higher temperature data with an empirical equation of the type recommended by KELLEY.(11)

The Debye and Einstein function sum proposed by KING(9) was modified to better fit our data. The equation

$$C_p = D(178/T)+3E(390/T)+3E(710/T)$$

fits our data to within 0·5 per cent over the range 130 to 300°K. This approximate lattice heat capacity is presented as a dashed curve in Fig. 1. Attempts to make a similar extrapolation from temperatures substantially lower than 130°K resulted in a calculated lattice heat capacity contribution in excess of the measured total value near 40°K. Hence the estimated value of the lattice contribution is almost certainly high over the entire range.

If the magnetic contribution is estimated as the difference of this and the experimental curve, the magnetic entropy is 2·2 cal/mole/deg. at 10°K, 4·0 at 25°K, and 4·5 at 150°K. The molal entropy increment between the completely disordered paramagnetic states and the ordered antiferromagnetic state is $2R\ln(2S+1) = 7\cdot12$ (cal/mole/deg). The discrepancy between the theoretical value and our rough estimate of the magnetic contribution can readily be explained if we assume the persistence of short range ordering contributions to the thermal properties above 130°K.

These data are thus seen to be in accord with the interpretation of HASTINGS and CORLISS(3) of the transition from paramagnetic zinc ferrite to an antiferromagnetic state at 9·5°K as a result of the spin interaction of the iron atoms. The anomalously high heat capacity above 9·5°K is consistent with the persistence of short range ordering above the Néel temperature and the interpretation of the diffuse scattering of neutrons observed at liquid nitrogen temperatures as arising from a short-range ferromagnetic interaction.

Note added in proof: The heat capacity here reported is consistent with the results calculated by TACHIKI and YOSIDA, *Progr. Theor. Phys., Osaka* **17,** 223 (1957).

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