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LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF ZINC FERRITES—II

EFFECT OF THERMAL HISTORY AND METALLIC ADDITIVES*

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Abstract—The heat capacities of annealed and quenched samples of $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$ and of quenched $ZnFe_2O_4$ have been determined over the range 5–350°K. Addition of lithium to zinc ferrite lowers the temperature of the co-operative thermal anomaly associated with antiferromagnetic ordering transition in accord with theory, and quenching of either material results in nearly complete disappearance of the λ-anomaly but modifies the pronounced high-temperature tail less significantly. The effects on the thermal properties are interpreted in terms of sublattice populations.

1. INTRODUCTION

ANNEALED zinc ferrite possesses the normal spinel structure. The zinc is located on the tetrahedrally co-ordinated A sites, and the iron on the octahedrally co-ordinated B sites.(1) As pointed out by NÉEL,(2) the transfer of the zinc from A to B sublattices can be described in terms of an energy increment, ω. When kT is considerably larger than ω, the zinc can be considered to be uniformly distributed among the various possible sites of both sublattices. The material would thus be partially inverted. With decreasing thermal agitation, the zinc should preferentially migrate to the A sites until, at 0°K, the material, after an infinite time, would be entirely normal. NÉEL(2) hypothesized that the energy ω is large and negative for manganese. It then numerically decreases with increasing atomic number and passes through zero between copper and zinc. He gave evidence to show that copper ferrite is partially inverted under suitable heat-treatment. BROCKMAN(3) pointed out that zinc ferrite could be made ferromagnetic by quenching from about 1400°C. According to the NÉEL(4) theory of ferrite magnetization, this would occur if the zinc were located partially on the B sublattice—a fact in agreement with a small positive energy increment for the transfer of zinc from the A to the B sublattice. The heat capacity of zinc ferrite (annealed) shows a sharp peak between 9·5 and 9·7°K.(5) This λ-type anomaly is due to a type of antiferromagnetic ordering of B sublattice iron moments.(6–8) The presence of a partial inversion, small deviations from stoichiometry, or foreign substances drastically effects the magnitude of the peak.(9,10) It was therefore decided to measure the specific heat of a sample deliberately partially inverted by water-quenching from 1100°C. The object was to determine if the effect complementary to the appearance of a magnetic moment at low temperatures, namely the disappearance of the 9·5°K heat-capacity peak, occurred. This was indeed observed.

Quenched and annealed samples of zinc ferrite containing small amounts of lithium were also prepared and measured. The analogous heat-capacity difference of the zinc ferrites was still present. Annealed lithium–zinc ferrite is considered particularly interesting because of the possibility of

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ordering of the lithium on the B sites.(11) This provides a possible means of inserting nonmagnetic ions into the B sublattice, while producing only limited modifying results due to molecular field fluctuations.(12)

2. EXPERIMENTAL

(a) *Preparation and purity of the samples*

The samples were prepared by the technique described for $ZnFe_2O_4$(5) except that two of these samples were quenched from 1100°C by immersion in distilled water. One sample was stoichiometric $ZnFe_2O_4$; two were mixed to the composition $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$. Quantitative analysis gave the results shown in Table 1.

Table 1. *Analysis of zinc ferrites*

Composition	Treatment	Percentage by Weight					
		Theoretical			Observed		
		Zn	Fe	Li	Zn	Fe	Li
$ZnFe_2O_4$	Annealed*	27·12	46·33	—	27·2	46·2	—
	Quenched	27·12	46·33	—	27·0	46·0	—
$Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$	Annealed	24·75	48·16	0·15	24·4	47·9	0·11
	Quenched				24·4	48·0	0·12

* Data on this specimen reported in reference (5).

(b) *Cryogenic technique*

The Mark I cryostat and the technique employed for low-temperature adiabatic calorimetry are described.(13)

The copper calorimeter (laboratory designation W-9) was similar to calorimeter W-6;(14) it was gold-plated inside and out, but had only four vanes. The specific heat of the empty calorimeter was separately determined (using the same thermometer and heater, and the same amounts of indium-tin solder for sealing and Apiezon-T grease for thermal contact with the thermometer and heater); it represented from 20 to 50 per cent of the total heat capacity observed. The platinum resistance thermometer (laboratory designation A-3) was calibrated at the National Bureau of Standards. The temperatures are believed to correspond with the thermodynamic scale within 0·03° from 10° to 90°K, and within 0·04° from 90° to 350°K. The individual measured temperature increments are probably accurate to a millidegree after corrections for quasi-adiabatic drift.

The calorimeter was loaded with sample, evacuated, filled with helium at 4 cm Hg pressure at 300°K (to provide thermal contact between calorimeter and sample), sealed, placed in the cryostat, and cooled over a period of several days to approximately 4°K. The weights of samples used were 209·950 g of $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$ (annealed), 213·331 g of quenched $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$, and 238·384 g of $ZnFe_2O_4$.

3. RESULTS

The heat-capacity determinations are listed in Table 2 in chronological order. The individual temperature increments can generally be estimated from the adjacent mean temperatures. The values are expressed in terms of the defined thermochemical calorie of 4·1840 absolute J.

The ice point is taken to be 273·15°K. The molecular or gram-formula weights of $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$ and $ZnFe_2O_4$ were taken to be 237·682 and 241·08, respectively. An analytically determined "curvature" correction for the finite temperature increments employed has been added to each observed value of $\Delta H/\Delta T$. Because of the low pressure in the calorimeter, the values thus corrected to dH/dT are equal to C_p° or C_{sat}° within the limits of the experimental error. Above 30°K, most of the points deviated from the curve by less than 0·001 cal/mole/°K; the deviations were not normally distributed and in a very few cases were close to 0·01 cal/mole/°K. Experience

Table 2. Molal heat capacities (C_p) of zinc and lithium-zinc ferrites (cal(deg.g.mole)$^{-1}$)

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
		$Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$			
Series I		*Series* I (*cont.*)		*Series* II (*cont.*)	
52·10	4·724	250·07	30·39	14·64	2·143
57·64	5·553	260·05	31·11	16·13	2·039
63·14	6·417	270·14	31·76	18·00	1·935
68·96	7·330	280·12	32·37	20·14	1·862
75·23	8·330	290·23	32·96	22·34	1·843
81·72	9·409	300·48	33·52	24·64	1·872
88·65	10·558	310·90	34·05	27·16	1·960
96·22	11·777	321·53	34·54		
104·29	13·076	332·39	35·03	*Series* III	
112·84	14·450	343·39	35·49	5·05	0·53
121·58	15·835			5·92	0·95
130·20	17·170			6·79	2·01
138·62	18·423	*Series* II		7·49	3·35
147·26	19·666	5·29	0·62	8·14	2·81
156·38	20·92	5·90	0·92	9·07	2·65
165·95	22·17	6·58	1·64	10·08	2·52
175·77	23·38	7·19	3·03	11·07	2·42
182·75	24·20	7·82	3·01	27·41	1·971
192·27	25·25	8·63	2·74	30·22	2·135
201·81	26·24	9·13	2·64	33·21	2·374
211·33	27·16	9·81	2·55	36·50	2·693
220·85	28·03	10·76	2·44	40·21	3·111
230·52	28·87	11·96	2·34	44·35	3·635
240·20	29·64	13·27	2·240	48·87	4·257

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
		Quenched $Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4$			
Series I		*Series* II (*cont.*)		*Series* III (*cont.*)	
97·48	12·764	8·70	1·30	8·76	1·31
106·78	14·280	9·76	1·37	9·66	1·37
116·58	15·826	10·95	1·42	10·58	1·41
125·95	17·315	12·20	1·447	11·61	1·46
135·26	18·730	13·43	1·483		
145·05	20·16	14·79	1·510	*Series* IV	
155·38	21·58	16·37	1·539	54·94	5·720
159·74	22·16	18·11	1·578	60·61	6·626
167·88	23·21	19·89	1·632	66·28	7·550
178·05	24·42	21·85	1·715	72·19	8·534
188·81	25·63	24·12	1·828	78·38	9·574
200·35	26·85	26·64	1·973	84·89	10·695
212·09	27·99	29·48	2·245	91·87	11·847
224·23	29·08	32·54	2·554	99·45	13·085
236·40	30·09	35·77	2·925	107·54	14·392
248·41	31·01	39·35	3·380	115·63	15·670
260·56	31·85	43·41	3·932		
272·60	32·63	48·08	4·635	*Series* V	
284·59	33·35	52·80	5·384	287·47	33·51
296·72	33·99			297·28	34·01
		Series III		307·03	34·49
Series II		5·29	0·58	316·67	34·98
5·81	0·73	6·08	0·80	326·27	35·39
6·91	1·01	6·99	1·02	335·96	35·79
8·51	1·27	7·86	1·18	345·79	36·19

Table 2 (continued)

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
		Quenched $ZnFe_2O_4$			
Series I		*Series* II (*cont.*)		*Series* IV (*cont.*)	
77·38	9·596	292·23	33·87	13·44	1·372
83·97	10·740	301·82	34·33	15·07	1·429
90·94	11·936	311·29	34·81	17·03	1·473
98·28	13·133	320·81	35·23	18·94	1·546
106·20	14·420	330·45	35·63	20·97	1·636
114·41	15·746	339·30	36·00	23·16	1·760
122·86	17·078	347·80	36·32	25·64	1·932
131·53	18·410			28·42	2·171
140·24	19·678			28·15	2·144
148·94	20·91	*Series* III		31·12	2·439
157·90	22·13	5·08	0·20	34·14	2·785
167·26	23·35	5·12	0·22	37·12	3·162
176·68	24·48	5·33	0·24	40·19	3·580
183·62	25·27	5·68	0·28	43·71	4·090
195·05	26·50	6·48	0·39	47·84	4·729
204·89	27·48	6·93	0·49	52·66	5·509
214·49	28·40	7·71	0·77	58·00	6·347
224·03	29·25	8·31	1·08	63·60	7·302
229·61	29·72	8·93	1·25	70·41	8·431
238·91	30·46	9·82	1·32	78·50	9·786
248·35	31·15	11·03	1·343	85·67	11·036
258·02	31·82	12·39	1·334		
		13·82	1·380		
Series II		15·35	1·428	*Series* V	
253·41	31·51			7·36	0·65
263·22	32·17			8·02	0·92
273·00	32·78	*Series* IV		8·77	1·21
282·63	33·34	12·18	1·330	9·74	1·31

indicated that these deviations are not reproducible and presumably not significant. Below 30°K the measurements become progressively less accurate due to the smaller absolute heat capacity, the smaller temperature intervals, and the decreased sensitivity of the thermometer. Below about 9°K, considerable time was required for the establishment of thermal equilibrium, as had been noted in the heat capacity of zinc ferrite.(5)

Values of C_p°, $S^\circ - S_0^\circ$, and $(H^\circ - H_0^\circ)/T$ at selected temperatures are presented in Tables 3, 4, and 5. The enthalpy and entropy increments were computed by numerical integration, using graphically interpolated values of heat capacity. The values of entropy are considered to be accurate to $\pm 0{\cdot}01$ eu, even at the higher temperatures, and the enthalpy values are considered accurate to $\pm 0{\cdot}1$ per cent, except at the lowest temperatures.

Some of the tabular data are given to an additional digit because, while it is not significant on an absolute basis, it is significant on a relative basis, as when the entropies or enthalpies at different temperatures are compared.

4. DISCUSSION

(*a*) $ZnFe_2O_4$

From the results given in Table 2 and depicted in Fig. 1, it is apparent that the quenching has eliminated all except elemental vestigia of the antiferromagnetic type ordering below 10°K. This is in agreement with the interpretation of sublattice population and spinel inversion as discussed by Néel(2) and evidenced by Brockman(3) utilizing the magnetic moment. The annealed zinc ferrite sample had a sharp peak of magnitude greater than 2·3*k* per iron atom. Although we were not able to establish an upper limit to the magnitude of the peak, it is probable that it is less than the 3·37*k* predicted by Tachiki and Yosida.(8) It is expected

Table 3. Molal thermodynamic functions for (annealed) lithium zinc ferrite ($\mathrm{Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4}$) *at selected temperatures*

T(°K)	C_p° (cal/deg. mole)	$S^\circ-S_0^\circ$ (cal/deg. mole)	$H^\circ-H_0^\circ$ (cal/mole)	$\frac{H^\circ-H_0^\circ}{T}$ (cal/deg. mole)
10	2·524	1·654	11·441	1·144
15	2·120	2·593	22·961	1·531
20	1·865	3·162	32·821	1·641
25	1·880	3·576	42·091	1·684
30	2·120	3·937	52·012	1·734
35	2·543	4·294	63·607	1·817
40	3·087	4·668	77·640	1·941
45	3·727	5·067	94·633	2·103
50	4·419	5·495	114·99	2·300
60	5·917	6·432	166·58	2·776
70	7·497	7·463	233·66	3·338
80	9·121	8·569	316·65	3·958
90	10·781	9·740	416·20	4·624
100	12·388	10·959	532·05	5·320
110	13·996	12·216	663·98	6·036
120	15·59	13·502	811·95	6·766
130	17·14	14·812	975·61	7·505
140	18·63	16·137	1154·23	8·245
150	20·05	17·471	1347·39	8·983
160	21·40	18·809	1554·68	9·717
170	22·69	20·15	1775·18	10·44
180	23·89	21·48	2008·12	11·16
190	25·01	22·80	2252·67	11·86
200	26·05	24·11	2508·04	12·54
210	27·04	25·40	2773·51	13·21
220	27·96	26·68	3048·52	13·86
230	28·83	27·94	3332·48	14·49
240	29·63	29·19	3624·77	15·10
250	30·39	30·41	3924·87	15·70
260	31·11	31·62	4232·39	16·28
270	31·76	32·81	4546·79	16·84
280	32·37	33·97	4867·45	17·38
290	32·94	35·12	5194·00	17·91
300	33·49	36·24	5526·18	18·42
350	35·76	41·58	7259·83	20·74
273·15	31·96	33·18	4647·14	17·01
298·15	33·39	36·04	5464·32	18·33

Table 4. Molal thermodynamic functions for quenched lithium zinc ferrite ($\mathrm{Li_{0\cdot05}Zn_{0\cdot90}Fe_{2\cdot05}O_4}$) *at selected temperatures*

T(°K)	C_p° (cal/deg. mole)	$S^\circ-S_0^\circ$ (cal/deg. mole)	$H^\circ-H_0^\circ$ (cal/mole)	$\frac{H^\circ-H_0^\circ}{T}$ (cal/deg. mole)
10	1·387	0·8698	3·47	0·3466
15	1·514	1·4599	10·76	0·7174
20	1·637	1·9099	18·60	0·9299
25	1·874	2·2994	27·35	1·0940
30	2·298	2·6745	37·67	1·2557
35	2·833	3·0675	50·45	1·4415
40	3·466	3·4867	66·18	1·6545
45	4·165	3·9345	85·22	1·9605
50	4·944	4·4131	107·97	2·1594
60	6·528	5·4541	165·30	2·7551
70	8·174	6·5833	238·76	3·4109
80	9·858	7·7831	328·8	4·1104
90	11·539	9·0425	435·9	4·8435
100	13·178	10·344	559·5	5·5954
110	14·780	11·676	699·4	6·358
120	16·388	13·031	855·3	7·127
130	17·940	14·404	1026·9	7·900
140	19·432	15·789	1213·9	8·671
150	20·86	17·178	1415·4	9·436
160	22·20	18·567	1630·8	10·192
170	23·47	19·952	1859·2	10·936
180	24·65	21·327	2103·0	11·684
190	25·76	22·689	2355·1	12·395
200	26·82	24·038	2618·0	13·090
210	27·80	25·371	2891·1	13·767
220	28·71	26·685	3173·7	14·426
230	29·57	27·980	3465·1	15·066
240	30·37	29·256	3764·9	15·687
250	31·12	30·511	4072·4	16·289
260	31·82	31·745	4387·1	16·873
270	32·47	32·958	4708·6	17·439
280	33·08	34·150	5036·3	17·987
290	33·64	35·321	5370·0	18·517
300	34·15	36·470	5709·1	19·030
350	36·33	41·908	7474·3	21·355
273·15	32·67	33·336	4811·2	17·614
298·15	34·06	36·259	5646·0	18·937

to be larger than the 2·36k given by their molecular field approximation. The measured value here is probably low because: (a) averages over finite temperature increments had to be measured and thus the numerical result must always be equal or less than the maximum, (b) the experimental procedure was difficult because of the large time lag in establishing thermal equilibrium, and (c) because our annealed sample was probably partially inverted. The reason for the latter is that the so-called Tammann temperature of zinc ferrite—the temperature for which body diffusion becomes negligible—is about 700°C. Although this is not a strict lower limit to the annealing temperature at which the zinc population can be in equilibrium between the two sublattices, it is improbable that the equilibrium would persist to a very much lower temperature. Thus the conditions at about 700°C would be frozen into the annealed specimen.

Table 5. *Molal thermodynamic functions for quenched zinc ferrite* ($ZnFe_2O_4$) *at selected temperatures*

T(°K)	$C_p°$ (cal/deg. mole)	$S°-S_0°$ (cal/deg. mole)	$H°-H_0°$ (cal/mole)	$\frac{H°-H_0°}{T}$ (cal/deg. mole)
10	1·327	0·532	3·99	0·039
15	1·418	1·081	10·77	0·718
20	1·591	1·510	18·25	0·913
25	1·886	1·894	26·88	1·075
30	2·325	2·275	37·35	1·245
35	2·892	2·674	50·34	1·438
40	3·556	3·103	66·43	1·661
45	4·289	3·563	86·02	1·912
50	5·067	4·055	109·42	2·188
60	6·693	5·121	168·08	2·801
70	8·366	6·279	243·41	3·477
80	10·046	7·505	335·4	4·192
90	11·780	8·789	444·6	4·940
100	13·409	10·115	570·6	5·706
110	15·037	11·470	712·8	6·480
120	16·633	12·847	871·2	7·260
130	18·182	14·240	1045·4	8·041
140	19·646	15·641	1234·5	8·818
150	21·06	17·045	1438·1	9·587
160	22·41	18·448	1655·5	10·347
170	23·69	19·845	1886·1	11·095
180	24·87	21·233	2128·9	11·827
190	25·98	22·608	2383·2	12·543
200	27·00	23·967	2648·2	13·241
210	27·98	25·308	2923·1	13·920
220	28·90	26·631	3207·5	14·580
230	29·75	27·935	3500·8	15·221
240	30·54	29·218	3802·4	15·843
250	31·27	30·480	4111·5	16·446
260	31·96	31·719	4427·6	17·029
270	32·60	32·937	4750·4	17·594
280	33·19	34·134	5079·4	18·141
290	33·75	35·309	5414·1	18·669
300	34·27	36·461	5754·2	19·181
350	36·41	41·911	7523·6	21·496
273·15	32·79	33·317	4853·4	17·768
298·15	34·17	36·250	5690·9	19·087

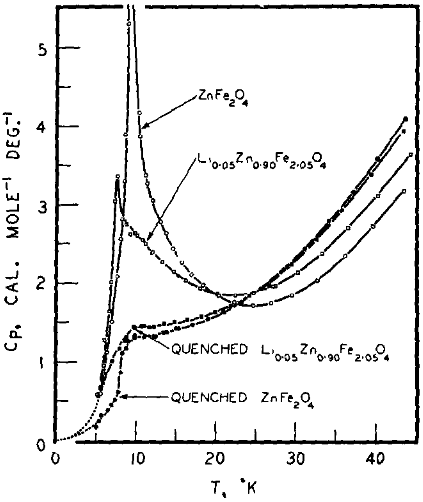

FIG. 1. The molal heat capacities of zinc ferrites at low temperature.

(b) $Li_{0.05}Zn_{0.90}Fe_{2.05}O_4$

Fig. 1 also illustrates the difference in heat capacity at low temperature of annealed and quenched mixed lithium–zinc ferrite of the composition considered in Table 1. The same general differences occur, but the height, shape, and temperature of the transition in the annealed specimen is different from either that of zinc or mixed nickel–zinc ferrite.(9)

Within the limits of experimental error, the additional 10 mol per cent $NiFe_2O_4$ leaves the $ZnFe_2O_4$ transition temperature unaltered, while 10 mol per cent $(LiFe)_{0\cdot5}Fe_2O_4$ lowers it some 20 per cent. This is true even though the nickel replaced 0·1 and the lithium 0·05 of the *B*-site iron.

This behavior difference appears to lie in either (*a*) that the Ni ion possesses a magnetic moment and the Li ion does not, or (*b*) that the Li ion forms an ordered substructure on the *B* sublattice. This has been demonstrated for annealed $(LiFe)_{0\cdot5}$ Fe_2O_4.(11) Hypothesis (*b*) is substantiated in that the temperature of the remanent heat capacity anomaly in the quenched lithium–zinc ferrite coincides with the 9·5° of zinc ferrite rather than the 7·6° anomaly of the annealed lithium–zinc ferrite.

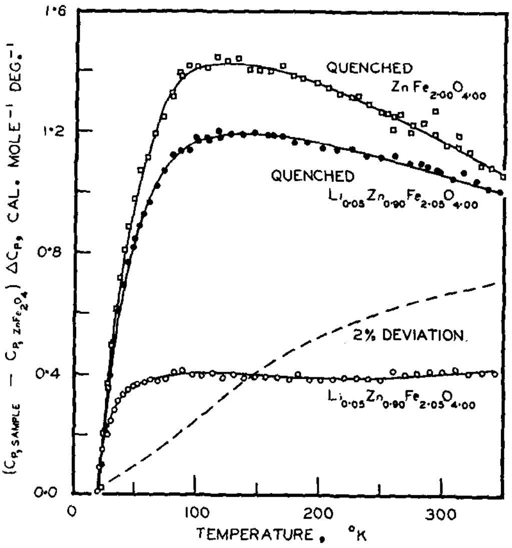

FIG. 2. The deviation of the molal heat capacities of zinc ferrites from those of zinc ferrite (annealed).

The thermal properties of $ZnFe_2O_4$ are thus seen to depend strongly upon thermal history, and may be interpreted in terms of sublattice populations. Small amounts of lithium considerably reduce the Néel temperature. It is suggested that the lithium goes onto the *B* sublattice to an ordered structure in a mixed zinc ferrite even when only 10 per cent of the available ordered lattice sites are occupied.

It is to be noted in Fig. 2 that not only are the deviations in thermal properties between quenched and annealed zinc ferrites pronounced in the vicinity of the anomaly, but are indeed significant over the entire temperature range studied. Thus between 50 and 100° in both compositions the heat capacity is about 10 per cent greater for quenched than for annealed samples. This increment decreases to about 4 per cent at 300°K. The importance of careful thermal treatment of samples of magnetic materials of the complexity of ferrospinels and transition-element chalcogenides is emphasized by these results. This is especially significant when such samples are to be used in the procurement of thermodynamic data. However, the comparison of the entropy increment at either 300 or 350°K reveals that $S^\circ - S_0^\circ$ of the two quenched compositions are identical within $\pm 0\cdot01$ eu. Those of the annealed materials are also nearly identical to each other, but 0·2–0·4 eu smaller than those of the quenched samples. Hence a 10 per cent lithium ferrite substitution in zinc ferrite does not significantly alter the total entropy increment nor apparently the magnetic entropy.

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