

# LOW-TEMPERATURE HEAT CAPACITIES AND THERMO-DYNAMIC PROPERTIES OF ZINC FERRITES—III

## EFFECT OF COPPER SUBSTITUTION

EDGAR F. WESTRUM, JR. and D. M. GRIMES

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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**Abstract**—The heat capacities of annealed and quenched samples of  $\text{Cu}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$  have been determined over the range 5–350°K. The Néel temperature is the same as that previously reported for a similar lithium-substituted zinc ferrite. The result is discussed in terms of the sublattice-population and molecular-field coefficients.

### 1. INTRODUCTION

THE low-temperature heat capacity and thermodynamic properties of zinc ferrite and of a solid solution of composition 90 mole per cent zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) and 10 mole per cent lithium ferrite ( $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ) have been studied and reported previously.<sup>(1)</sup> The data were taken on samples which, after forming spinels from the constituent oxides, had been annealed and on similar samples which had been quenched from 1100°C in distilled water. It was found<sup>(2)</sup> that the annealed samples had  $\lambda$ -type anomalies in the vicinity of 9°K. This effect has been associated with an antiferromagnetic-type ordering in zinc ferrite.<sup>(3)</sup> The heat-capacity curve for the quenched samples showed inflections at about 9°K, but a local maximum did not exist. These effects were explained on the basis of sublattice populations and freezing in the 1400°K population equilibrium by the water quench. Similar experimental data have now been obtained on other samples of quenched and annealed ferrite. The samples were solid solutions of composition 90 mole per cent zinc ferrite and 10 mole per cent copper ferrite ( $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ). The copper ferrite was prepared in such a way that, according to STIERSTADT,<sup>(4)</sup> it should be in the univalent state.

### 2. EXPERIMENTAL

The samples were prepared as described previously<sup>(2)</sup>, except that a Szegvari mixer was used in

place of the ball mill. The results of chemical analyses on the samples for iron and copper are shown in Table 1.

Table 1. Analyses of copper-zinc ferrites

Sample treatment	Percentage by weight			
	Observed		Theoretical	
	Cu	Fe	Cu	Fe
Annealed	1.33	47.68	1.32	47.60
Quenched	1.29	47.37	1.32	47.60

The cryogenic technique was as described previously,<sup>(2,5)</sup> except that calorimeter of laboratory designation W-10 was employed for these measurements. This calorimeter is similar to calorimeter W-9 previously described,<sup>(2)</sup> but has a slightly greater volume and lacks heat-conduction vanes. The masses of the calorimetric samples were 187.486 g of annealed and 166.54 g of quenched  $\text{Cu}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$ . The gram-molecular weight was taken to be 240.51 g.

### 3. RESULTS

The values of heat capacity, corrected for "curvature" and in terms of the defined thermochemical calorie of 4.1840 absolute J, and an ice point of 273.15°K are presented in Table 2. The

discussion of precision and intrinsic errors of the previous work<sup>(1,2)</sup> applies equally to the present results. Values of the heat capacity at selected temperatures, together with the standard entropy increment and enthalpy function, are presented for the two samples in Tables 3 and 4.

#### 4. DISCUSSION

The results at temperatures above 20°K are depicted graphically in Fig. 1, as the deviation of

A major difference between the copper- and the lithium-containing ferrites is that the copper can migrate between sublattices at the temperature of firing, while the lithium cannot. Moreover, the mass of the copper is much greater than that of the lithium. Table 5 shows the idealized sublattice populations in terms of the ferric ions and the closed-shell ions.

The slight difference in absolute value of heat capacity between annealed lithium- and copper-

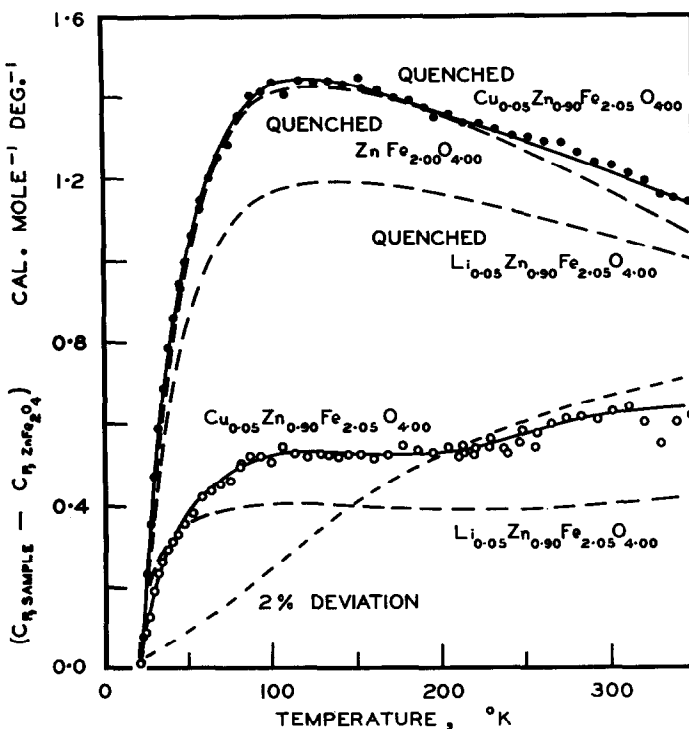


FIG. 1. The deviation of the heat capacities of copper-zinc and lithium-zinc ferrites from those of annealed zinc ferrite.

the heat capacities of the measured ferrites from those of annealed zinc ferrite. Only the smooth curve for the lithium-zinc ferrites and for the quenched zinc ferrite are shown; the curves for the copper-zinc ferrites are shown with the data points representing the actual determinations. The most striking characteristic of the curves is that, for the quenched samples, the copper-zinc ferrite resembles closely in properties the zinc ferrite itself, while the annealed copper-zinc ferrite more nearly resembles the lithium-zinc ferrite.

containing ferrites is not explicable on the basis of the idealized sublattice populations. It might be due, however, to differences in the lattice heat capacity, to imperfect ordering of the copper-containing ferrite, to the presence of divalent copper or to different values of exchange coefficients.

Within experimental error, and certainly within 0.1°K, the temperature of the anomalous peak is the same in both annealed lithium-containing and in annealed copper-containing ferrites (cf. Fig. 2).



Table 3. Molal thermodynamic functions for annealed copper-zinc ferrite ( $\text{Cu}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$ ) at selected temperatures

$T(^{\circ}\text{K})$	$C_p$ (cal/deg. mole)	$S^{\circ}-S_0^{\circ}$ (cal/deg. mole)	$H^{\circ}-H_0^{\circ}$ (cal/mole)	$H^{\circ}-H_0^{\circ}$	$T(^{\circ}\text{K})$	$C_p$ (cal/deg. mole)	$S^{\circ}-S_0^{\circ}$ (cal/deg. mole)	$H^{\circ}-H_0^{\circ}$ (cal/mole)	$H^{\circ}-H_0^{\circ}$
				$T$ (cal/deg. mole)					$T$ (cal/deg. mole)
10	2.554	1.297	9.954	0.995	170	22.82	19.882	1788.1	10.518
15	2.121	2.245	21.56	1.437	180	24.03	21.221	2022.4	11.235
20	1.844	2.810	31.36	1.568	190	25.15	22.551	2268.3	11.938
25	1.852	3.218	40.49	1.620	200	26.20	23.868	2525.1	12.625
30	2.094	3.573	50.27	1.676	210	27.18	25.170	2792.0	13.295
35	2.522	3.927	61.75	1.764	220	28.09	26.455	3068.3	13.947
40	3.077	4.299	75.70	1.893	230	28.97	27.724	3353.7	14.581
45	3.720	4.697	92.66	2.059	240	29.79	28.974	3647.5	15.198
50	4.429	5.126	113.0	2.260	250	30.53	30.206	3949.2	15.797
60	5.978	6.069	165.0	2.749	260	31.25	31.417	4258.1	16.377
70	7.569	7.109	232.7	3.324	270	31.94	32.609	4574.0	16.941
80	9.218	8.227	316.6	3.957	280	32.57	33.783	4896.6	17.488
90	10.85	9.407	419.5	4.661	290	33.17	34.936	5225.3	18.018
100	12.49	10.635	536.2	5.362	300	33.73	36.070	5559.8	18.533
110	14.10	11.901	669.2	6.083	350	35.98	41.449	7305.8	20.874
120	15.71	13.198	818.2	6.819	273.15	32.14	32.981	4674.4	17.113
130	17.25	14.516	983.1	7.562	298.15	33.63	35.861	5497.6	18.439
140	18.76	15.850	1163.2	8.308					
150	20.17	17.193	1357.9	9.052					
160	21.52	18.538	1566.3	9.790					

However, the transition temperature is lower in the lithium-containing ferrite than in a nickel-containing zinc ferrite.<sup>(2)</sup> One of the differences noted was that annealed lithium ferrite without zinc forms an ordered array of lithium ions on the *B* sublattice. Such is not the case for copper ferrite, yet the transition temperature is the same in copper- as in lithium-containing zinc ferrite. Therefore, it is concluded that the decrease in transition temperature is not due to intrasublattice ionic ordering.

The presence of divalent copper would require a change in oxidation state in some other ferrite constituent for a fixed oxygen content. The most probable ion to change oxidation state is, of course, ferric iron. Both divalent copper and divalent iron ions possess permanent magnetic moments, as does divalent nickel. The fact that the annealed copper-containing sample has a transition similar to the lithium-containing sample in both anomaly shape and temperature and not to the nickel-containing

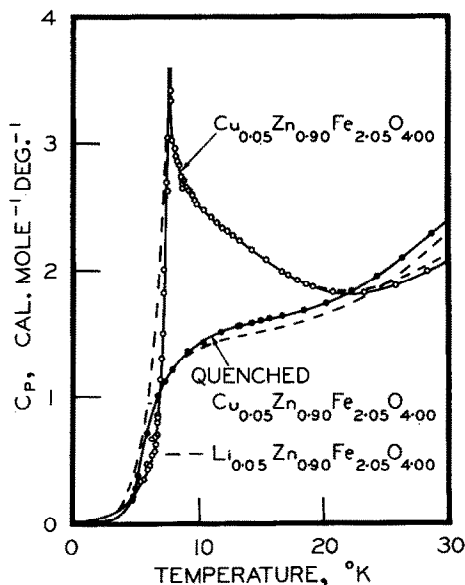


FIG. 2. The heat capacities of zinc ferrites at low temperatures.

Table 4. Molal thermodynamic functions for quenched copper-zinc ferrite ( $\text{Cu}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$ ) at selected temperatures

$T(^{\circ}\text{K})$	$C_p$ (cal/deg. mole)	$S^{\circ}-S_0^{\circ}$ (cal/deg. mole)	$H^{\circ}-H_0^{\circ}$ (cal/mole)	$H^{\circ}-H_0^{\circ}$	$T(^{\circ}\text{K})$	$C_p$ (cal/deg. mole)	$S^{\circ}-S_0^{\circ}$ (cal/deg. mole)	$H^{\circ}-H_0^{\circ}$ (cal/mole)	$H^{\circ}-H_0^{\circ}$
				$T$ (cal/deg. mole)					$T$ (cal/deg. mole)
10	1.428	0.834	5.873	0.587	170	23.69	20.363	1893.6	11.139
15	1.607	1.455	13.55	0.903	180	24.88	21.751	2136.5	11.869
20	1.730	1.932	21.86	1.093	190	25.98	23.126	2390.8	12.583
25	1.998	2.344	31.13	1.245	200	27.02	24.486	2655.9	13.279
30	2.410	2.743	42.08	1.403	210	27.99	25.828	2931.0	13.957
35	2.964	3.155	55.47	1.585	220	28.90	27.151	3215.5	14.616
40	3.612	3.592	71.88	1.797	230	29.76	28.455	3508.8	15.256
45	4.329	4.058	91.70	2.038	240	30.56	29.738	3810.4	15.877
50	5.098	4.554	115.3	2.305	250	31.30	31.001	4119.8	16.479
60	6.728	5.626	174.3	2.905	260	31.99	32.242	4436.3	17.063
70	8.386	6.788	249.9	3.570	270	32.62	33.461	4759.4	17.627
80	10.08	8.017	342.2	4.277	280	33.22	34.659	5088.6	18.174
90	11.78	9.302	451.5	5.017	290	33.78	35.835	5423.6	18.702
100	13.43	10.630	577.6	5.776	300	34.31	36.989	5764.0	19.213
110	15.04	11.984	719.9	6.544	350	36.48	42.448	7536.2	21.532
120	16.64	13.361	878.3	7.319	273.15	32.82	34.841	4862.4	17.801
130	18.18	14.754	1052.4	8.095	298.15	34.21	36.777	5700.6	19.120
140	19.67	16.156	1241.6	8.869					
150	21.08	17.562	1445.4	9.636					
160	22.43	18.965	1662.9	10.393					

sample indicates further that the copper is monovalent.

The ferritic compound is considered as  $\text{Me}_x\text{Zn}_{1-2x}\text{Fe}_{2+x}\text{O}_4$  where Me represents a univalent nonmagnetic ion such as those of Li or Cu. The ferrite is assumed to consist of two  $B$  sublattices,  $B^+$  and  $B^-$ , and a single  $A$  sublattice. For annealed samples the Me ions are assumed to be randomly distributed on the  $B$  sublattice. The governing equations in the nonordered state are (by an extension of the treatment of TACHIKI and YOSIDA<sup>(6)</sup>):

$$\left. \begin{aligned} TM_{B^+} &= [1-(x/2)]C_{B^+}[H-(x/2)M_{B^+}-\alpha M_{B^-}-\beta M_A] \\ TM_{B^-} &= [1-(x/2)]C_{B^-}[H-\alpha M_{B^+}-(x/2)M_{B^-}-\beta M_A] \\ TM_A &= 2xC_A[H-\beta M_{B^+}-\beta M_{B^-}-\gamma M_A]. \end{aligned} \right\} \quad (1)$$

It will be assumed that the Lande  $g$ -factors are equal, i.e.  $g_{B^+} = g_{B^-} = g_A$ , so  $C_{B^+} = C_{B^-} = C_A$ . The condition that a nontrivial solution of equa-

tions (1) exists when  $H = 0$  is that the determinant of the coefficients of the  $M$ 's be zero. The resulting cubic equation contains the root,

$$T = \frac{\alpha C}{2} \left(1 - \frac{x}{2}\right), \quad (2)$$

which is independent of the magnitudes of  $\beta$  and  $\lambda$ .

If the moments on the  $A$  sublattice are considered to be resolved into two sublattices, the treatment of YAFET and KITTEL<sup>(7)</sup> is applicable. Their result for the antiferromagnetic ordering

temperature on the  $B$  sublattice,  $T_{C2}$ , reduces to equation (2) above.

For the ferrites measured,  $x = 0.05$ , so the ratio

Table 5. Idealized sublattice populations

Sublattice	Ion	Zn ferrite	Li-Zn ferrite	Cu-Zn ferrite
<i>Annealed samples</i>				
A	R*	1.00	0.90	0.90
	Fe	0	0.10	0.10
B	R	0	0.05	0.05
	Fe	2.00	1.95	1.95
<i>Quenched samples</i>				
A	R	0.333	0.305	0.317
	Fe	0.667	0.695	0.683
B	R	0.667	0.645	0.633
	Fe	1.333	1.355	1.367

\* R = ions with zero intrinsic moment.

of Néel temperatures in the mixed ferrites to that in the zinc ferrite, for constant  $\alpha$ , is 0.975. The measured ratio was 0.8. If the difference is attributed to variations of  $\alpha$  with  $x$ , it should be noted that the shift in  $\alpha$  is the same for  $\text{Li}^{+1}$  (radius of 0.78 Å) and  $\text{Cu}^{+1}$  (radius of 0.96 Å).

The magnetic moments of the quenched samples at 0°K are, ideally, the moments of 0.667, 0.660 and 0.684 ferric ions per formula for zinc, mixed lithium-zinc and mixed copper-zinc ferrites, respectively. Since the dependence of the magnetic moment upon temperature is not known as a function of  $x$ , it is not possible to correlate the moments with the heat-capacity curve at present.

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