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LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF ZINC FERRITES---III EFFECT OF COPPER SUBSTITUTION

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ABSTRACT

The heat capacities of annealed and quenched samples of $Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4$ have been determined over the range 5-350°K. The Néel temperature is the same as previously reported for a similar lithium-substituted zinc ferrite. The result is discussed in terms of sublattice popluation 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 percent zinc ferrite ($ZnFe_2O_4$) and 10 mole percent lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$) have been studied and reported previously.[1] 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[2] that the annealed samples had λ-type anomalies in the vicinity of 9°K. This effect has been associated with an antiferromagnetic-type ordering in zinc ferrite.[3] 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 ferrites. The samples were solid solutions of composition 90 mole percent zinc ferrite and 10 mole percent copper ferrite ($CU_{0.5}Fe_{2.5}O_4$). The copper ferrite was prepared in such a way that according to Stierstadt[4] it would be in the univalent state.

2. EXPERIMENTAL

The samples were prepared as described previously,[2] 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	Percent 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,[2,5] except that calorimeter of laboratory designation W-10 was employed for these measurements. This calorimeter is similar to calorimeter W-9 previously described,[2] 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 $Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4$. 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[1,2] apply 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 Table 3 and 4.

4. DISCUSSION

The results at temperatures above 20°K are depicted graphically in Fig. 1, as the deviation of 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 the properties of zinc ferrite itself, while the annealed copper-zinc ferrite more nearly resembles the lithium-zinc ferrite.

Table 2. Heat Capacities of Copper-Zinc Ferrites

in cal(deg g mole)$^{-1}$

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
		(Annealed) $\mathrm{Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4}$			
Series I		7.16	2.01	39.26	2.990
		7.34	2.70	42.38	3.374
211.01	27.29	7.72	3.33	46.18	3.888
219.18	28.03	8.03	2.96	51.17	4.607
228.15	28.83	8.23	2.86	56.68	5.460
237.29	29.56	8.39	2.83	62.28	6.337
246.28	30.31	8.53	2.74	67.90	7.239
255.09	30.93	8.66	2.72	73.75	8.178
		8.81	2.71	80.15	9.246
Series II		8.96	2.66		
		9.14	2.64	Series VI	
131.98	17.56				
137.33	18.36	Series IV		5.33	0.34
143.72	19.30			5.84	0.43
150.86	20.30	5.53	0.35	6.20	0.53
158.54	21.33	6.01	0.46	6.50	0.62
167.02	22.44	6.63	0.80	6.62	0.71
175.75	23.53	7.09	1.50	6.88	1.13
184.33	24.52	7.69	3.42	7.46	2.63

Table 2 (continued)

193.49	25.52	8.10	2.90	7.82	3.02
202.80	26.49	8.65	2.65	8.09	2.96
211.90	27.36	9.46	2.60	8.64	2.69
208.95	27.07	10.08	2.550	9.23	2.631
217.89	27.90	10.53	2.495	9.87	2.571
226.90	28.71	11.18	2.454	10.52	2.502
235.95	29.47	11.97	2.350	11.12	2.460
245.10	30.20	12.78	2.297	11.58	2.419
254.46	30.85	Series V		12.25	2.332
263.88	31.55			13.22	2.262
273.13	32.15	5.24	0.34	14.22	2.168
282.23	32.70	5.78	0.47	15.40	2.086
291.36	33.22	6.20	0.67	16.67	1.994
300.67	33.71	6.69	0.86	17.95	1.921
310.12	34.23	7.13	1.82	19.17	1.870
319.62	34.65	7.38	3.05		
329.21	35.04	7.76	3.33	Series VII	
338.90	35.50	17.19	1.964		
347.53	35.87	18.64	1.889	79.46	9.130
		20.80	1.826	85.46	10.144
Series III		23.32	1.821	91.50	11.133
		25.88	1.879	97.88	12.161
6.46	0.67	28.42	1.994	104.90	13.343
6.49	0.69	31.07	2.173	112.02	14.449
6.67	0.84	33.76	2.402	119.26	15.60
6.96	1.30	36.45	2.673	127.28	16.85

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
		Quenched $Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4$			
Series I		51.49	5.333	86.43	11.183
		56.42	6.147	93.32	12.320
93.82	12.402				
99.48	13.356	Series III		Series IV	
106.98	14.539				
115.57	15.91	7.23	1.12	152.30	21.39
124.36	17.31	10.34	1.43	161.81	22.66
133.17	18.66	11.75	1.518	171.34	23.86
142.05	19.96	13.31	1.569	180.63	24.95
151.03	21.22	14.99	1.608	189.73	25.96
		16.71	1.640	195.16	26.52
Series II		18.45	1.685	203.90	27.42
		20.29	1.739	212.90	28.26
4.82	0.28	22.31	1.836	222.17	29.09
13.18	1.56	24.37	1.957	231.74	29.90
14.24	1.59	26.39	2.098	241.26	30.66

Table 2 (continued)

15.68	1.62	28.73	2.291	250.88	31.37
4.57	0.19	31.35	2.547	260.78	32.04
4.68	0.22	34.15	2.860	270.55	32.67
5.04	0.38	37.25	3.247	280.48	33.25
5.71	0.72	40.49	3.681	290.44	33.80
6.67	1.01	43.95	4.177	300.44	34.34
7.83	1.21	56.27	6.108	310.47	34.82
9.07	1.36	61.73	7.015	320.38	35.28
44.10	4.193	67.27	7.942	329.06	35.64
47.32	4.682	73.38	8.943	336.67	35.96
		79.84	10.047	345.33	36.31

Table 3. Molal thermodynamic functions for (annealed) copper-zinc ferrite ($Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4$) at selected temperatures

T(°K)	C_p (cal/deg. mole)	$S^o-S^o_0$ (cal/deg. mole)	$H^o-H^o_0$ (cal/ mole)	$\frac{H^o-H^o_0}{T}$ (cal/deg. mole)
10	2.554	1.297	9.954	0.995
15	2.121	2.245	21.56	1.437
20	1.844	2.810	31.36	1.568
25	1.852	3.218	40.49	1.620
30	2.094	3.573	50.27	1.676
35	2.522	3.927	61.75	1.764
40	3.077	4.299	75.70	1.893
45	3.720	4.697	92.66	2.059
50	4.429	5.126	113.0	2.260
60	5.978	6.069	165.0	2.749
70	7.569	7.109	232.7	3.324
80	9.218	8.227	316.6	3.957
90	10.85	9.407	419.5	4.661
100	12.49	10.635	536.2	5.362
110	14.10	11.901	669.2	6.083
120	15.71	13.198	818.2	6.819
130	17.25	14.516	983.1	7.562
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

Table 3 (continued)

170	22.82	19.882	1788.1	10.518
180	24.03	21.221	2022.4	11.235
190	25.15	22.551	2268.3	11.938
200	26.20	23.868	2525.1	12.625
210	27.18	25.170	2792.0	13.295
220	28.09	26.455	3068.3	13.947
230	28.97	27.724	3353.7	14.581
240	29.79	28.974	3647.5	15.198
250	30.53	30.206	3949.2	15.797
260	31.25	31.417	4258.1	16.377
270	31.94	32.609	4574.0	16.941
280	32.57	33.783	4896.6	17.488
290	33.17	34.936	5225.3	18.018
300	33.73	36.070	5559.8	18.533
350	35.98	41.449	7305.8	20.874
273.15	32.14	32.981	4674.4	17.113
298.15	33.63	35.861	5497.6	18.439

Table 4. Molal thermodynamic functions for quenched copper-zinc ferrite ($Cu_{0.05}Zn_{0.90}Fe_{2.05}O_4$) at selected temperatures

T(°K)	C_p (cal/deg. mole)	$S^o-S^o_0$ (cal/deg. mole)	$H^o-H^o_0$ (cal/mole)	$\frac{H^o-H^o_0}{T}$ (cal/deg. mole)
10	1.428	0.834	5.873	0.587
15	1.607	1.455	13.55	0.903
20	1.730	1.932	21.86	1.093
25	1.998	2.344	31.13	1.245
30	2.410	2.743	42.08	1.403
35	2.964	3.155	55.47	1.585
40	3.612	3.592	71.88	1.797
45	4.329	4.058	91.70	2.038
50	5.098	4.554	115.3	2.305
60	6.728	5.626	174.3	2.905

Table 4. (continued)

70	8.386	6.788	249.9	3.570
80	10.08	8.017	342.2	4.277
90	11.78	9.302	451.5	5.017
100	13.43	10.630	577.6	5.776
110	15.04	11.984	719.9	6.544
120	16.64	13.361	878.3	7.319
130	18.18	14.754	1052.4	8.095
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
170	23.69	20.363	1893.6	11.139
180	24.88	21.751	2136.5	11.869
190	25.98	23.126	2390.8	12.583
200	27.02	24.486	2655.9	13.279
210	27.99	25.828	2931.0	13.957
220	28.90	27.151	3215.5	14.616
230	29.76	28.455	3508.8	15.256
240	30.56	29.738	3810.4	15.877
250	31.30	31.007	4119.8	16.479
260	31.99	32.242	4436.3	17.063
270	32.62	33.461	4759.4	17.627
280	33.22	34.659	5088.6	18.174
290	33.78	35.835	5423.6	18.702
300	34.31	36.939	5764.0	19.213
350	36.48	42.448	7536.2	21.532
273.15	32.82	34.841	4862.4	17.801
298.15	34.21	36.777	5700.6	19.120

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.

Table 5. Idealized Sublattice Populations

Sublattice	Ion	Zn Ferrite	Li-Zn Ferrite	Cu-Zn Ferrite
		Annealed Samples		
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
		Quenched Samples		
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.

The slight difference in absolute value of heat capacity between annealed lithium- and copper-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). However, the transition temperature is lower in the lithium-containing ferrite than in a nickel-containing zinc ferrite.[2] 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 sample indicates further that the copper is monovalent.

The ferritic compound is considered as $Me_xZn_{1-2x}Fe_{2+x}O_4$ 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^6):

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

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 equations (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,

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

which is independent of the magnitudes of β and γ.

If the moments on the A sublattice are considered to be resolved into two sublattices, the treatment of Yafet and Kittel[7] is applicable. Their result for the antiferromagnetic ordering temperature on the B sublattice, T_{C2}, reduces to Eq. (2) above.

For the ferrites measured, x = .05, so the ratio of Néel temperatures in the mixed ferrites to that in the zinc ferrite, for constant α, is 0.975. The measured ratio was 0.8. If the difference is attributed to variations of α with x, it should be noted that the shift in α is the same for Li^{+1} (radius of 0.78 A) and Cu^{+1} (radius of 0.96 A).

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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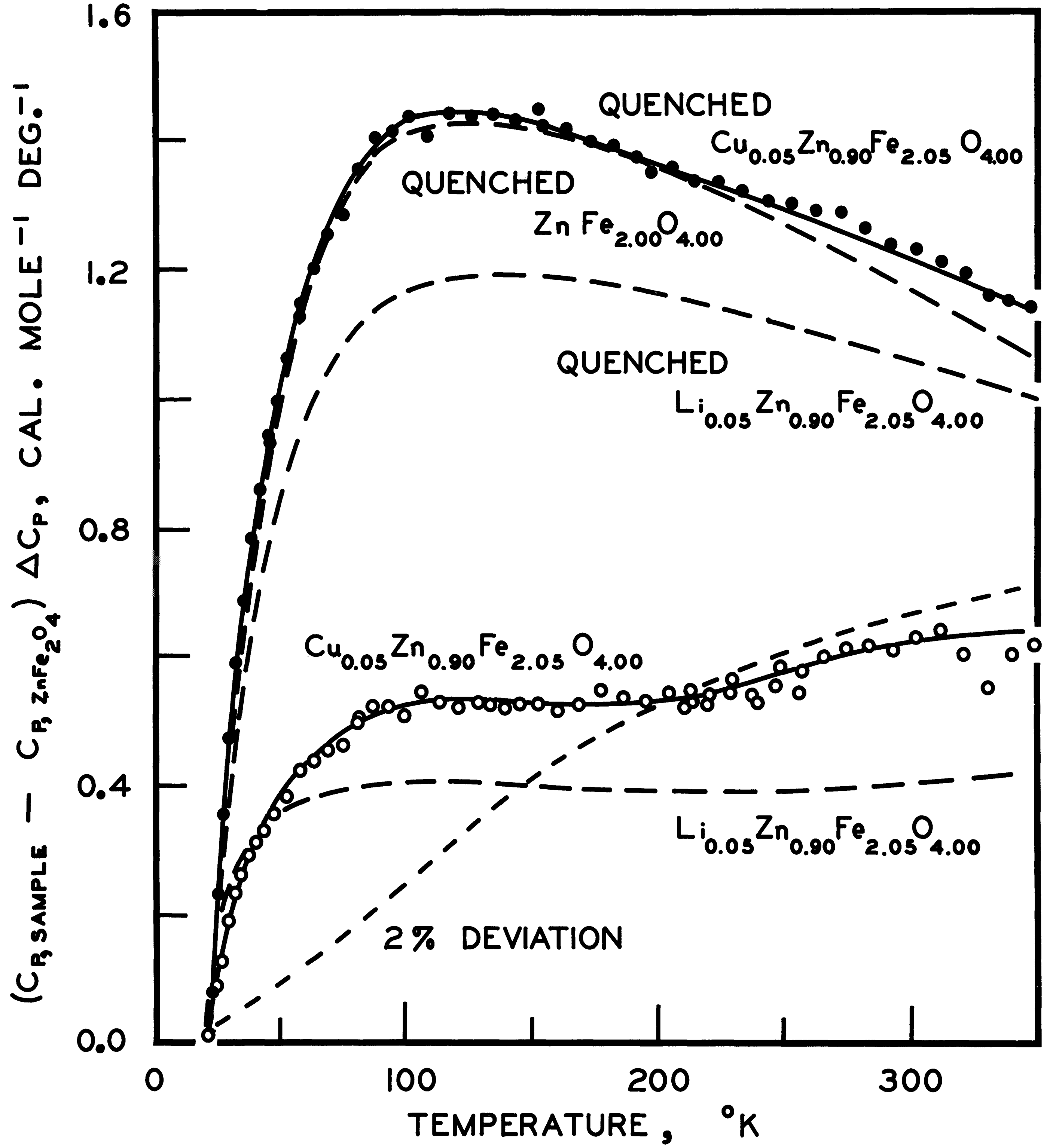

Fig. 1. The deviation of the heat capacities of copper-zinc and lithium-zinc ferrites from those of (annealed) zinc ferrite.

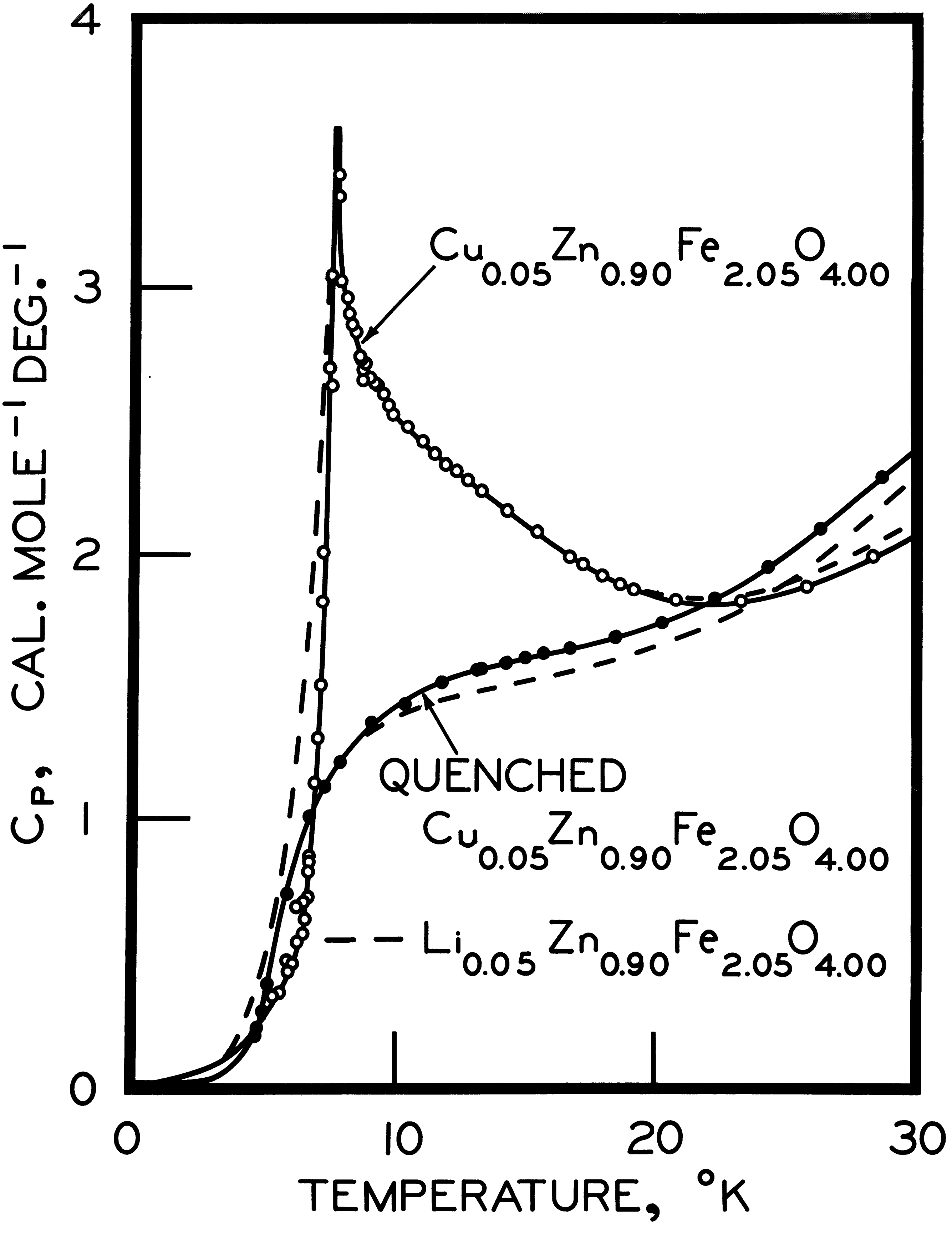

Fig. 2. The heat capacities of zinc ferrites at low temperatures.

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