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HEAT CAPACITIES AT LOW TEMPERATURES, ENTROPY AND ENTHALPY INCREMENTS OF
FOUR NICKEL ZINC FERROSPINELS

By Edgar F. Westrum, Jr., and D. M. Grimes

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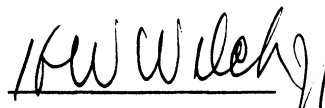
LOW TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ZINC FERRITE

By Edgar F. Westrum, Jr., and D. M. Grimes

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FOREWORD

This report is actually three related reports bound under one cover. They are copies of manuscripts submitted to the Journal of Physical Chemistry, Physical Review and the Journal of Physics and Chemistry of Solids respectively. It is expected that the appendix will be filed with the American Documentation Institute.

ABSTRACT

The heat capacity and the magnetic moment versus temperature of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ has been measured from about 4°K to 300°K where $x = .9, .8, .7,$ and $.6$. The heat capacity has been measured over the same temperature range for ZnFe_2O_4 . An antiferromagnetic cooperative transition at about 9.5° K was observed in ZnFe_2O_4 which gradually becomes more rounded and contributes less entropy as x decreases. The magnetic moment decreases gradually with increasing temperature and for the larger values of x goes slowly towards zero in marked contrast to the usual Curie temperature behavior. The results are interpreted as being due to molecular field fluctuations. Predicted thermal effects due to triangular-ferrimagnetic transitions were not found. This result is also interpreted in terms of molecular field fluctuations.

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I. INTRODUCTION

Spinel materials are fairly common and include important ores. Synthetic ferros spinels (ferrites) possess interesting electromagnetic properties and are technologically significant components of high frequency electrical circuits. Despite these facts, thermal data extending to liquid helium temperatures, which permit a more accurate evaluation of the thermodynamic properties of the ferrites are available probably only for zinc ferrite (ZnFe_2O_4).¹ Heat capacity data above 50°K . have, however, been published for more than twelve others,² and measurements on magnetite over the range 1.8 to 4.2°K . have recently been published.³

The gross magnetic properties of the ferros spinels have been explained by Néel⁴ in terms of the parallel and antiparallel alignment of the magnetic moments of the ions on two sublattices. For instance, in nickel ferrite (NiFe_2O_4) the net spin of the zinc ion is zero and the iron atoms are paramagnetic at this temperature. Mixed nickel-zinc ferrites are ferrimagnetic with a magnetic moment increasing with nickel content over the range studied. For certain ratios of inter- to intra-sublattice interactions, it is anticipated by Yafet and Kittel⁵ that the moments of two sub-sublattices composing one of the sublattices will be oriented neither parallel nor antiparallel with each other, but at some intermediate angle. The existence of such a triangular configuration would give rise to the possibility of transitions between triangular and ferrimagnetic or antiferromagnetic states

and hence to singularities analogous to Curie and Néel points. Utilizing an experimental evaluation of the exchange interactions by Néel and Brochet⁶ for mixed nickel-zinc ferrites ($\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$), Yafet and Kittel⁵ predicted the possible existence of such multiple transitions in mixed nickel-zinc ferrites with $x \geq 0.7$.

Such transitions should be readily detected at low temperatures by precise heat capacity determinations, for the discontinuities associated with the various types of transitions are well within the range of measurement of modern adiabatic, cryogenic calorimetry. The thermal method has the advantage of avoiding the spurious effects in magnetic measurements occasioned by ferromagnetic impurities. To test the theory of Yafet and Kittel, determination of the heat capacity of Ferramic E, a commercially available ferrite with x approximating 0.6, was first measured. Although no evidence of the anticipated spectrum of transformations was observed, the composition was indeed outside the range specified by Yafet and Kittel⁵. A ferrite of composition $x = 0.8$ was then fabricated and its heat capacity determined. An anomalously high heat capacity in the vicinity of 10°K . provoked further measurements on additional samples over the range $x = 0.6$ to $x = 1.0$. In conjunction with neutron diffraction data⁷ it has been established that this anomaly arises as a consequence of an antiferromagnetic-ordering which occurs in pure zinc ferrite.² Although resolution of the magnetic and lattice components of the heat capacity is not yet possible, the thermodynamic data are presented as a contribution to the thermodynamics of solid solutions.

II. PREPARATION AND PURITY OF SAMPLES

Mixed nickel-zinc ferrites, the composition of which may be represented by the empirical formula $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, with $x = 0.6, 0.7, 0.8$ and 0.9 , were prepared by milling a slurry of weighed quantities of chemically pure oxides in

a steel ball mill for six hours. After drying, the mixture was pressed into 50 gram slugs and fired at 1200°C. for four hours in air and the temperature then reduced 60°C./hr. to about 400°C. in an oxygen atmosphere. The slugs were fragmented in a hardened-steel "diamond mortar," annealed in an oxygen atmosphere and cooled at a rate of 60°C./hr.

Because of the strong dependence of the heat capacity in the vicinity of 10°K. upon composition as x approaches unity, especially great care was taken in the preparation technique to obtain a stoichiometric, homogeneous, non-inverted sample of zinc ferrite. The details of the fabrication procedure utilized are described elsewhere.¹ Gravimetric chemical analyses for iron and zinc and spectrochemical analyses were made. Stannous chloride redox titrations were made to determine the ferrous iron content of the samples. X-ray diffraction photographs were taken to establish the phase purity of the samples. The analytical data are presented in Table I.

TABLE I
PREPARATIVE AND ANALYTICAL DATA ON FERRITE SAMPLES

Sample x =	Annealing Temp. (°C.)	Percent Iron		Percent Fe ⁺⁺
		Detected	Theoretical	
(0.6) ^a	-	46.9 ± 0.1		0.0 ± 0.1
0.6	900	46.8 ± 0.1	46.84	0.0 ± 0.1
0.7	(1200)			0.1 ± 0.1
0.8	1200	46.7 ± 0.1	46.59	0.0 ± 0.1
0.9	(1200)			0.0 ± 0.1
1.0 ^b	1100	46.24 ± 0.1	46.33	0.0 ± 0.1

a Ferramic E, General Ceramic and Steatite Corp.

b Percent zinc found = 27.2 ± 0.1 (theoretical, 27.12).

III. CRYOGENIC TECHNIQUE

The design and adiabatic method of operation of the Mark I cryostat⁸ and calorimeters W-5⁹ and W-9¹⁰ have been described. A calorimeter was in turn loaded with sample, evacuated, and 2 to 4 cm. of gaseous helium then added at 25°C. to aid in the establishment of thermal equilibrium. Lubri-Seal stopcock grease was used on calorimeter W-5 for thermal contact between heater, thermometer and calorimeter for determinations on samples with $x = 0.6$ and 0.8 and on Ferramic E. Calorimeter W-9 with Apiezon T grease was employed for the balance of the runs to allow measurements to 350°K. Separate determinations of the heat capacity of the empty calorimeters were made with their respective conductivity greases. The following masses (vacuo) of samples were employed in the measurements: $x = 0.6$, 203.434 g. ; $x = 0.7$, 164.515 g.; $x = 0.8$, 191.862 g.; $x = 0.9$, 180.265 g.

Temperatures were determined with a capsule-type platinum resistance thermometer (Laboratory Designation A-3) contained in a central well in the calorimeter. It was calibrated by the National Bureau of Standards from 10° to above 373°K. Below this temperature range a provisional scale was employed. It is considered that the thermometer reproduces the thermodynamic temperature scale within 0.1° from 4 to 10°K., within 0.03° from 10 to 90°K., and within 0.05° above 90°K. The ice point was taken as 273.16°K. Calibrated instruments were used in the determination of all the measured quantities including the timing of the energy input.

IV. HEAT CAPACITY RESULTS

The experimental heat capacity determinations for the four samples of ferrospinels synthesized in this laboratory are presented in Table II in

TABLE II

MOLAL HEAT CAPACITIES OF NICKEL ZINC FERROSPINELS
(in calories degree⁻¹ gram-mole⁻¹)

T, °K.	C _p	T, °K.	C _p	T, °K.	C _p
Ni _{0.4} Zn _{0.6} Fe ₂ O ₄ (Mol. Wt. = 238.404 gm.)					
Series I		219.59	29.73	10.00	0.2317
		228.65	30.61	11.11	0.2569
63.23	6.324	237.58	31.41	12.38	0.2950
69.11	7.354	246.56	32.19	13.77	0.3415
75.83	8.556	255.62	32.91	15.27	0.4018
83.16	9.900	264.65	33.62	16.86	0.4653
91.49	11.418	273.70	34.30	18.52	0.5393
90.54	11.255	282.71	34.92	20.28	0.6274
98.30	12.613	291.70	35.52	22.17	0.7363
106.78	14.100	300.83	36.09	24.37	0.8862
115.28	15.589			26.80	1.073
123.12	16.933	Series II		29.37	1.304
130.70	18.189			32.14	1.591
138.60	19.456	4.50	0.068	35.29	1.956
147.06	20.77	4.87	0.066	38.67	2.394
155.74	22.06	5.65	0.085	42.16	2.879
164.52	23.30	4.75	0.070	46.10	3.468
173.47	24.51	5.58	0.082	50.74	4.204
182.58	25.65	5.49	0.080	55.57	5.003
191.87	26.77	6.66	0.105	60.34	5.818
201.18	27.83	7.87	0.142	65.57	6.376
210.40	28.83	8.96	0.184		
Ni _{0.3} Zn _{0.7} Fe ₂ O ₄ (Mol. Wt. = 239.073 gm.)					
Series I		237.48	31.21	335.70	37.43
		247.58	32.07	345.83	37.84
35.79	2.522	257.62	32.86		
39.51	2.997	267.72	33.59	Series III	
48.00	4.276	277.94	34.29		
53.47	5.202	288.21	34.92	5.71	0.142
58.77	6.093	298.73	35.55	6.58	0.188
64.43	7.079	309.38	36.16	7.59	0.300
70.56	8.133	319.94	36.77	8.56	0.376
77.46	9.330			9.47	0.444
84.48	10.608	Series II		10.33	0.4923
91.47	11.826			11.30	0.5186
99.32	13.152	173.08	24.45	12.41	0.5713

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TABLE II (CONTINUED)

107.50	14.567	182.60	25.62	13.65	0.6353
115.56	15.917	192.25	26.75	15.10	0.7055
123.76	17.273	201.97	27.81	16.75	0.7946
132.32	18.646	211.82	28.84	18.55	0.8878
140.88	19.962	221.95	29.81	20.42	1.0014
149.47	21.25	232.37	30.76	22.32	1.1307
158.52	22.52	242.87	31.68	24.43	1.2913
168.10	23.82	253.32	32.51	27.06	1.5209
177.84	25.07	263.78	33.29	30.05	1.8177
187.66	26.25	274.26	34.02	33.43	2.208
197.62	27.38	284.62	34.70	36.94	2.660
207.21	28.38	294.90	35.34	40.31	3.132
207.31	28.38	305.22	35.93	44.10	3.690
217.42	29.38	315.47	36.48	48.11	4.324
227.23	30.32	325.60	36.94		

$Ni_{0.2}Zn_{0.8}Fe_2O_4$ (Mol. Wt. = 239.742 gm.)

4.95	0.152	33.87	2.581	156.53	22.17
5.45	0.154	37.27	3.023	165.21	23.31
5.94	0.269	41.13	3.561	174.01	24.46
6.55	0.438	45.42	4.196	182.75	25.48
7.49	0.578	49.92	4.913	191.53	26.46
8.70	0.721	54.87	5.728	200.38	27.42
9.91	0.846	60.66	6.694	209.27	28.30
11.17	0.8773	67.19	7.809	210.47	28.41
12.50	0.9387	73.80	8.934	219.36	29.23
14.02	1.010	80.35	10.086	228.17	30.00
15.66	1.091	87.37	11.326	237.02	30.73
17.35	1.174	95.11	12.623	245.89	31.46
19.15	1.266	103.38	14.045	254.64	32.08
21.05	1.383	112.09	15.437	263.23	32.71
23.15	1.529	121.39	16.956	271.68	33.23
25.46	1.705	130.54	18.392	280.14	33.76
27.98	1.932	139.40	19.736	288.75	34.25
30.76	2.218	148.06	21.01	297.66	34.71

$Ni_{0.1}Zn_{0.9}Fe_2O_4$ (Mol. Wt. = 240.411 gm.)

Series I		12.56	1.6665	94.52	12.191
		13.71	1.6839	101.80	13.372
6.22	0.330	15.33	1.6961	109.70	14.646
6.48	0.494	17.28	1.7102	118.99	16.123
7.08	0.688	19.34	1.7375	128.10	17.544
7.76	1.29	21.37	1.7923	136.30	18.770
8.54	1.53	23.49	1.8782	144.47	19.950
9.29	1.62	25.88	2.008	153.07	21.15
10.00	1.7283	28.31	2.175	162.33	22.37

TABLE II (CONTINUED)

11.32	1.6868	30.90	2.400	172.04	23.58
		33.91	2.706	181.55	24.70
Series II		37.40	3.111	190.90	25.73
		41.55	3.650	200.43	26.72
5.66	0.353	46.25	4.319	210.27	27.67
5.93	0.543	51.44	5.109	220.43	28.59
6.27	0.584	56.87	5.958	230.85	29.48
6.59	0.647	61.98	6.800	241.44	30.32
6.98	0.764	67.43	7.686	252.14	31.10
7.43	1.000	73.39	8.662	262.75	31.82
7.89	1.21	80.18	9.809	273.26	32.48
8.28	1.37	87.50	11.050	283.77	33.10
8.73	1.50	95.15	12.296	294.16	33.68
9.23	1.63			304.19	34.20
9.75	1.72	Series III		314.78	34.74
10.33	1.7323			324.97	35.15
10.90	1.6768	80.54	9.866	335.16	35.59
11.61	1.6651	87.37	11.023	345.44	35.98

TABLE III

MOLAL ENTROPY AND ENTHALPY INCREMENTS OF NICKEL-ZINC FERROSPINELS

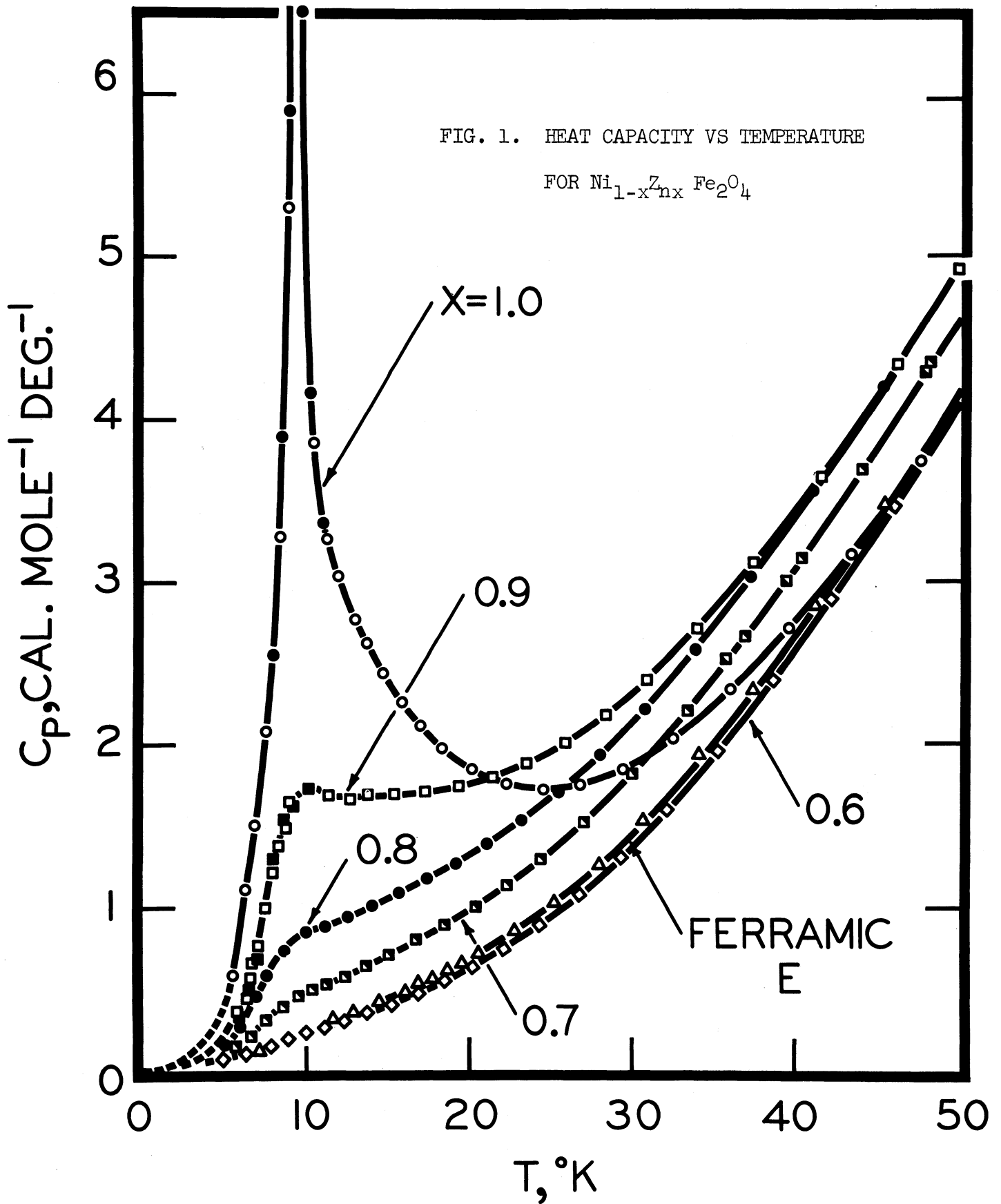
T, °K.	x = 0.6	x = 0.7	x = 0.8	x = 0.9
$S^{\circ} - S_0^{\circ}$				
(in calories degree ⁻¹ gram-mole ⁻¹)				
10	0.077	0.156	0.196	0.737
15	0.197	0.388	0.574	1.419
25	0.507	0.880	1.243	2.322
50	1.995	2.701	3.283	4.438
100	7.501	8.544	9.298	10.317
200	21.392	22.533	23.275	23.929
300	34.362	35.416	35.960	36.291
298.16	34.140	35.196	35.746	36.082
$H^{\circ} - H_0^{\circ}$				
(in calories gram-mole ⁻¹)				
10	0.58	1.50	2.87	5.42
15	2.09	4.40	7.58	13.84
25	8.39	14.30	20.92	31.63
50	66.59	84.65	99.18	112.15
100	489.11	531.2	557.7	559.8
200	2579.0	2632.6	2655.3	2602.8
300	5806.5	5837.0	5809.0	5675.9
298.16	5740.3	5771.5	5745.0	5613.5

chronological sequence so that the temperature increments of the individual runs can be estimated from the adjacent mean temperatures. Corrections for curvature (occasioned by the finite temperature increments employed in the measurements) and for the slight differences in the amounts of helium and solder in the measurements on the empty and the full calorimeters have been applied. The data are presented in terms of the defined thermochemical calories of 4.1840 absolute joules and the formula (molal) weight in grams using 1953 International Atomic Weights.

Heat capacities below 50°K. are presented in Fig. 1. Figure 2 compares the heat capacities at higher temperatures with the smooth curve for zinc ferrite¹ in order to amplify the small differences between these curves. On both plots the points indicated represent the individual determinations, and the heat capacities of Ferramic E and zinc ferrite¹ have been included for comparison. The significant features are: (1) the sharp transition due to antiferromagnetic ordering in zinc ferrite at about 9.5°K. which obviously persists in the mixed ferros spinels at approximately the same temperature, but decreases in intensity with increasing nickel content; and (2) the absence of other peaks or fluctuations in the curves. No singularities of the type predicted by Yafet and Kittel⁵ were observed. The ferrimagnetic contributions to the thermal properties cannot at present be quantitatively resolved from those of the lattice.

V. THERMODYNAMIC FUNCTIONS

The entropies and enthalpy increments computed by numerical quadrature from large scale plots of the heat capacity are provided at selected temperatures in Table III. Nuclear spin and isotope mixing contributions have not been included in the entropy. Extrapolation below about 5°K. was made with the Debye limiting law. The estimated probable error in the entropy increment is ± 0.06 e.u., and



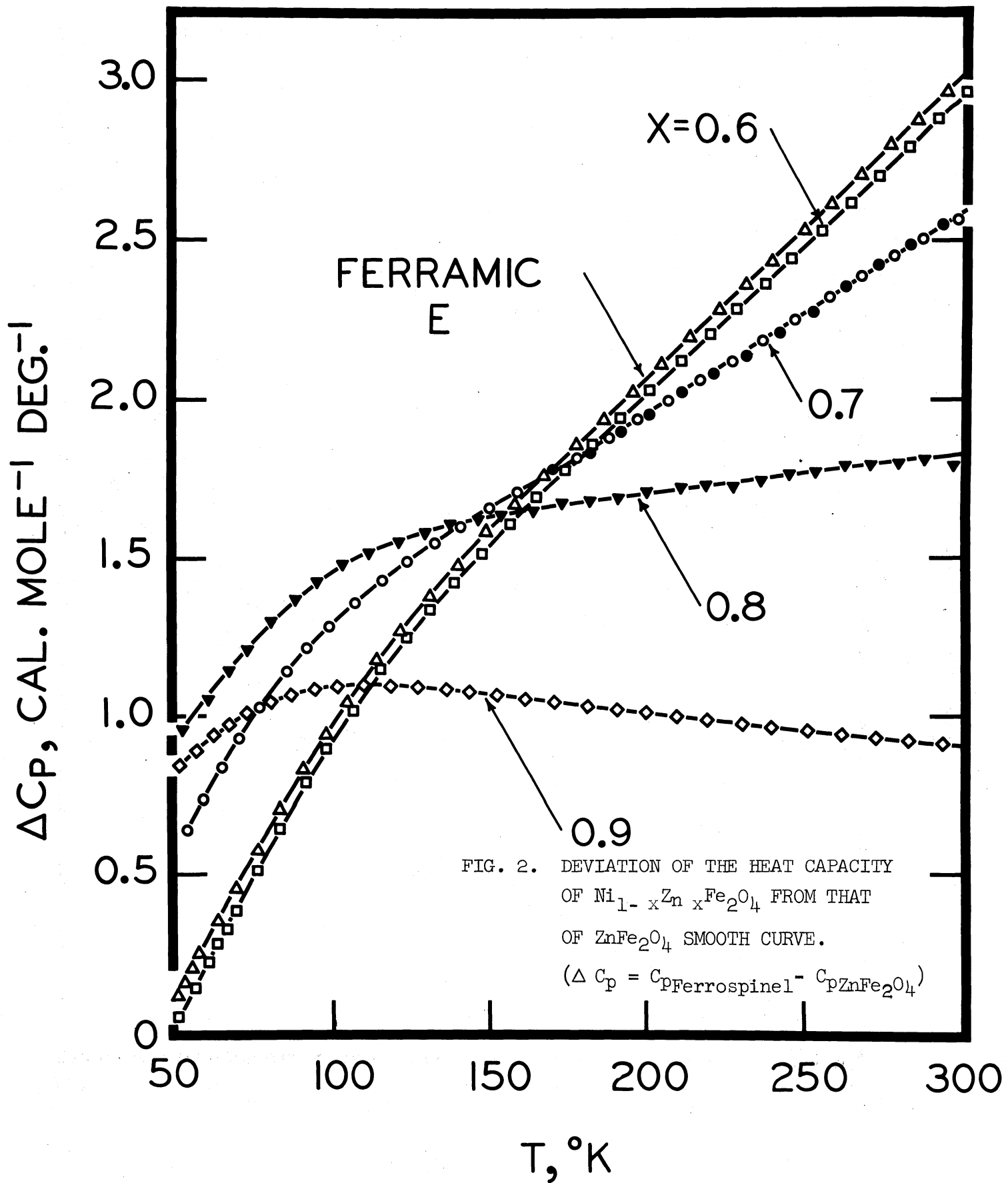


FIG. 2. DEVIATION OF THE HEAT CAPACITY OF $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ FROM THAT OF ZnFe_2O_4 SMOOTH CURVE.

$$(\Delta C_p = C_{p\text{Ferrosipinel}} - C_{p\text{ZnFe}_2\text{O}_4})$$

in the enthalpy increment is $\pm 0.1\%$. More extensive tabulation of the temperature dependence of the thermodynamic functions of these four ferrites have been prepared.¹¹

If the nickel ions occupy B sites and zinc ions occupy A sites, then the configuration entropy resulting from mixing zinc and iron ions at random on the A sites is given by:

$$S_A = -R \ln x^x(1-x)^{1-x}$$

and the configurational entropy resulting from mixing zinc and iron atoms at random on the B sites is given by:

$$S_B = -R \ln 4^{-1} (1-x)^{1-x}(1+x)^{1+x} .$$

The sum of these two expressions represents an upper bound to the zero-point entropy and amounts to 0.72 R, 1.15 R, and 1.46 R and 1.67 R for $x = 0.9, 0.8, 0.7$ and 0.6 , respectively. The actual entropy at 0°K . will be less than the above due to the mutual ordering effects of the A and B sublattices by the electrical interactions between them.

REFERENCES

1. E. F. Westrum, Jr. and D. M. Grimes, (Paper submitted to Physics and Chemistry of Solids).
2. E. G. King, J. Chem. Phys., 60, 410 (1956). Cf. the references to other works contained therein.
3. J. S. Kouvel, Phys. Rev., 102, 1489 (1956).
4. L. Néel, Ann. Phys., 3, 137 (1948).
5. Y. Yafet and C. Kittel, Phys. Rev., 87, 290 (1952).
6. L. Néel and P. Brochet, Compt. rend., 230, 280 (1950).
7. J. M. Hastings and L. M. Corliss, Phys. Rev., 102, 1460 (1956); Rev. Mod. Phys., 25, 114 (1953).
8. E. F. Westrum, Jr. and A. F. Beale, Jr., (to be published).
9. G. A. Burney and E. F. Westrum, Jr., (to be published).
10. E. Greenberg and E. F. Westrum, Jr., J. Am. Chem. Soc., 78, 4526 (1956).
11. Extensive tabulation of the heat capacities, enthalpy and entropy increments and enthalpy function of these four ferros spinels in addition to heat capacity data on Ferramic E are listed in the Appendix.

MOLECULAR FIELD FLUCTUATION EFFECTS IN MIXED NICKEL ZINC FERRITES

By D. M. Grimes, S. Legvold, and Edgar F. Westrum, Jr.

Both nickel and zinc ferrites have spinel structures; the lattice constants are not greatly different and the two ferrites are completely soluble in each other. Each zinc cation in zinc ferrite (ZnFe_2O_4) carries zero net electronic spin and is situated at the center of a tetrahedron of oxygen ions. The array of all such sites occupied in the perfect lattice is called the A sublattice. The iron cations occupy sites surrounded by an octahedron of oxygen ions. The array of octahedral sites occupied in the perfect lattice forms the B sublattice. For nickel ferrite (NiFe_2O_4), the nickel carries two net spins and occupies the B sites while the iron occupies all the A sites and one-half of the B sites. For the case of mixed nickel zinc ferrites it is presumed that the nickel goes always on the B sites and the zinc always on the A sites. The questions of the distribution of the nickel on the B sublattice and, in the case of mixed ferrites, of the distribution of the zinc on the A sublattice have been discussed by Néel¹ and Smart,² and it is concluded that the nickel probably is randomly arrayed on the B sublattice² and that the zinc on the A sublattice is also randomly arrayed for the mixed ferrites. However, electrical charge considerations would tend to establish some correlation on the atomic scale between local A and B sublattice populations.

The magnetic properties of the ferrimagnetic ferrites (e.g. mixed nickel zinc ferrites) are usually explained by stating that the exchange interactions can be described in terms of effective molecular fields which have their origin in the net spins of the constituent atoms. Each sublattice

is treated as a homogeneous unit and the problem is considered solved when the constant molecular field coefficients corresponding to the A-A, B-B and A-B interactions are known.

For a small concentration, $(1-x)$, of NiFe_2O_4 in ZnFe_2O_4 , there will be $(1-x)$ iron ions on the A sites among the nonmagnetic zinc ions. This can be considered as a basically nonmagnetic lattice with interspersed regions of high magnetic intensity. For such a model the concept of only three applicable molecular field coefficients is no longer valid and the portion which can be retained will depend upon the smallest defineable unit of a particular ferrite. Thus when $(1-x)$ is zero the material will obviously be zinc ferrite, but as $(1-x)$ increases the regions surrounding the A site iron will be a mixed ferrite, the rest a mesh of zinc ferrite. The magnitude of $(1-x)$ for which this heterogeneous model is valid will depend upon the smallest defineable unit of zinc ferrite. Since regions rich in iron would be ferrimagnetic while other regions poorer in iron would not, ferrimagnetic regions immersed in an antiferromagnetic or paramagnetic mesh would result. As the temperature is lowered the fraction of the material in the ferrimagnetic regions increases at the expense of the fraction in the nonmagnetic mesh. Thus the concept of a single Curie temperature becomes meaningless. Although the magnitude of the smallest units of volume which can be considered to be zinc ferrite, or can be considered as a given mixed ferrite, can not be unambiguously resolved; the assumption of particular smallest units involving only nearest neighbor interactions permits a calculation to be made. The qualitative effect of such regions can be seen from the temperature dependence of the magnetic moment of mixed nickel zinc ferrites for ferrites rich in zinc. Figure 1 shows data taken on material of the composition $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ where x has the values of 0.9, 0.8, 0.7 and 0.6. Note that as the temperature increases the

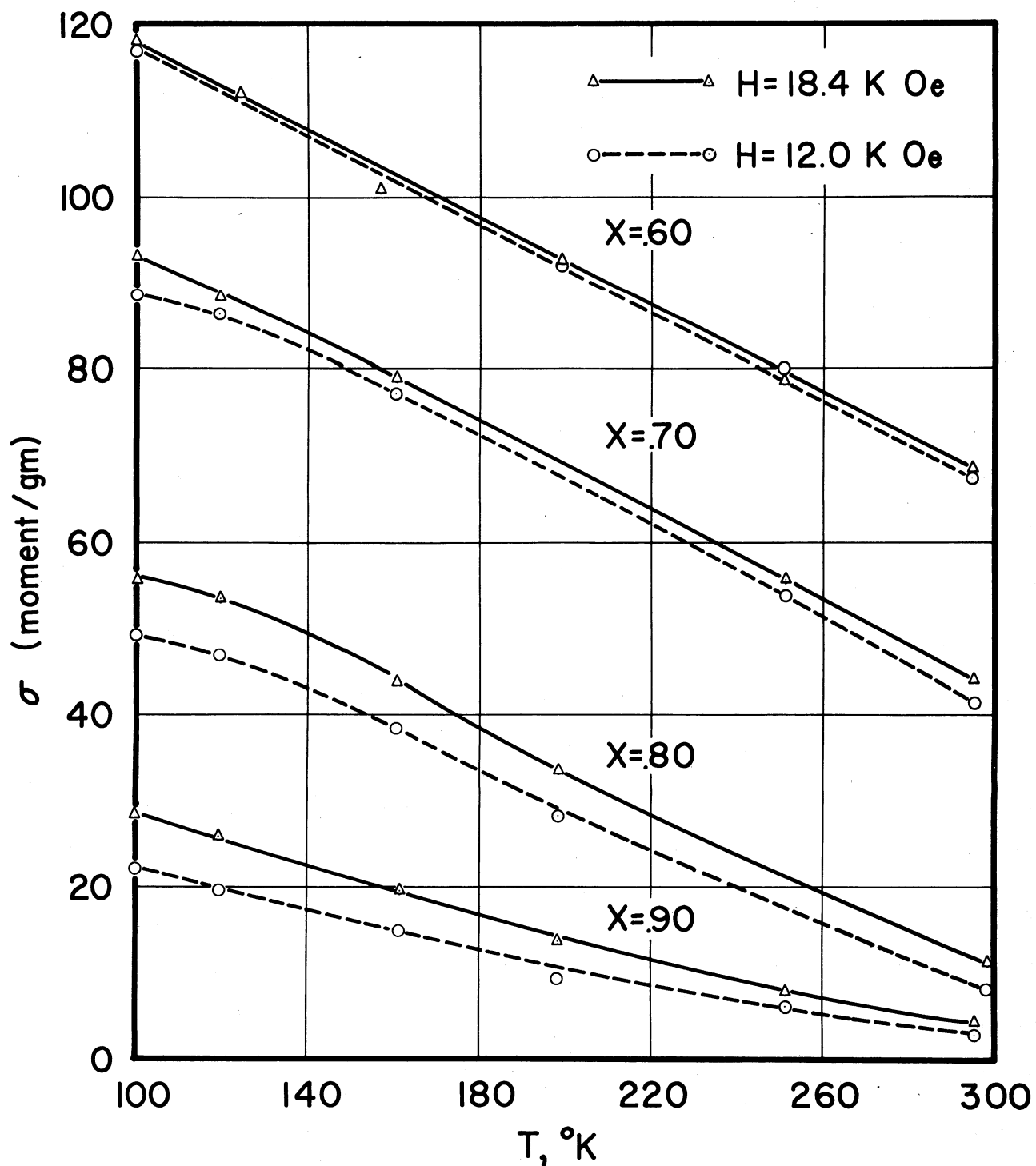


FIG. 1 MAGNETIC MOMENT VS. TEMPERATURE
 FOR $Zn_xNi_{1-x}Fe_2O_4$

magnetic moment decreases gradually for the larger values of x . The experimental technique for obtaining the magnetic data has been described.³

A complementary effect can be seen in the heat capacity of the same materials. Zinc ferrite undergoes a type of antiferromagnetic ordering just below 10° K.⁴ Thus for the case of the mixed ferrites, if some smallest unit of zinc ferrite can be considered, then any larger units of zinc ferrite will contribute to the anomalous heat capacity but material in the neighborhood of A site iron ions will not undergo this transition. The variation in the heat capacity as a function of temperature for several values of the variable x has been presented.⁵

It was shown by Yafet and Kittel⁶ that the two sublattice model for describing the magnetic properties of the ferrimagnetic ferrites, under certain conditions, violates the so-called third law of thermodynamics. They showed that this violation would no longer occur if each of the sublattices were further subdivided into two sub-lattices. They also pointed out, from extrapolation of existing data⁷ for the molecular field interaction coefficients of mixed nickel zinc ferrites of high nickel content, that the four sublattice model should give rise to magnetic transitions, for about the composition $\text{Ni}_{.2}\text{Zn}_{.8}\text{Fe}_2\text{O}_4$ not predicted by the two sublattice model. Although they should be observable by modern cryogenic techniques, existing heat capacity data⁵ show no such transitions. It must be expected, however, that even if such transitions did take place the molecular field fluctuations would result in transition temperatures which vary throughout the material. Hence the heat capacity effect would be spread over a temperature range and, as such, probably not observable.

It must be expected that the distribution of effective molecular fields would affect other structure insensitive magnetic properties such as the effective anisotropy. This would in turn affect the relaxation frequency of the material,

which is proportional to the effective anisotropy field in many cases, and give rise to a relaxation frequency varying from spot to spot in the material. Such effects are, of course, observed.⁸ However many other factors such as magnetic interactions among grains also produce differing relaxation frequencies so the experimental measurement of this relaxation spread is not considered to be necessarily a verification of fluctuations in the molecular fields.

REFERENCES

1. L. Néel, Ann. l'Inst. Fourier 1, 163 (1950).
2. J. S. Smart, Phys. Rev. 94, 847 (1954).
3. Elliott, Legvold, Spedding, Phys. Rev. 91, 28 (1953).
4. E. F. Westrum, Jr. and D. M. Grimes, Submitted to J. Phys. Chem. Solids
5. E. F. Westrum, Jr. and D. M. Grimes, Submitted to J. Phys. Chem.
6. Y. Yafet and C. Kittel, Phys. Rev. 87, 290 (1952).
7. L. Néel and P. Brochet, Compt. rend. 230, 280 (1950).
8. D. Park, Phys. Rev. 97, 60 (1955); 98, 438 (1955).

LOW TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ZINC FERRITE

By Edgar F. Westrum, Jr. and D. M. Grimes

I. 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 octahedral sites as tetrahedral sites in the spinel structure, half of the trivalent iron atoms also occupy octahedral 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 ferros spinels 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 ferrites¹ of empirical formula $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ over the range $x = 0.6$ to $x = 0.9$ 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 Hasings and Corliss³ confirm the existence of this transition and strongly suggest that it results from an antiferromagnetic type of ordering.

However, the thermal anomaly reported by Friedberg⁴ in zinc ferrite is considerably rounded and broadened compared to other cooperative 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 cooperative transitions might be expected as a consequence of partial inversion of the "normal" spinel structure, of inhomogeneity on the atomic scale, or of deviation from exact 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.

II. EXPERIMENTAL

2.1 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 indicated¹, great care was exercised in the preparative technique to obtain, as nearly as possible, a stoichiometric, homogeneous, non-inverted sample of zinc ferrite.

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Equimolal quantities of weighed, anhydrous, chemically pure ZnO and Fe₂O₃ 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 hours. 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 hours, and gradually allowed to cool in the furnace to 30°C over a period of 16 hours. The resulting ferrite granules were of a uniform reddish-brown color throughout.

Gravimetric chemical determinations showed $46.24 \pm 0.1\%$ iron (theoretical: 46.33) and $27.2 \pm 0.1\%$ zinc (theoretical: 27.12). Spectrochemical analyses revealed 0.01 to 0.1% of Al and Mn and 0.001 to 0.01% of Ca, Cu, Mg, Ni, and Si. Stannous chloride redox titration indicates less than 0.1% ferrous iron in the samples.

2.2 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-6⁶ 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 dunction 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 well. A

150-ohm 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 thermometers⁷ over the range $10\text{-}90^{\circ}\text{K}$.

Below 10°K we established a provisional temperature scale by fitting the constants in the equation⁸ $R = A + BT^2 + CT^5$ 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 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.

III. RESULTS

The experimental values of the observed molal heat capacity of zinc ferrite are presented in Table I. 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. 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.

TABLE I

 MOLAL HEAT CAPACITY OF ZINC FERRITE
 (in calories degree⁻¹ gram-mole⁻¹)

T, °K	C _p	T, °K	C _p	T, °K	C _p
Series I		10.18	4.17	36.01	2.341
184.44	24.00	10.91	3.37	39.61	2.716
193.52	25.00	Series III		43.47	3.176
203.27	25.99			47.72	3.740
212.90	26.93	5.50	0.58	52.45	4.413
222.68	27.80	6.24	1.11	Series IV	
232.53	28.65	6.82	1.50	17.04	2.123
242.39	29.43	7.48	2.08	18.69	1.957
252.28	30.16	8.46	3.28	52.37	4.298
262.21	30.85	8.89	5.3	58.05	5.246
272.28	31.44	9.39	(8.7)	64.00	6.173
282.53	32.10	9.75	(8.3)	69.98	7.115
292.86	32.71	10.38	3.86	76.16	8.097
303.14	33.25	11.10	3.272	82.61	9.183
313.31	33.77	11.82	3.034	89.79	10.335
323.41	34.23	12.95	2.787	97.61	11.608
333.65	34.66	13.66	2.635	105.53	12.900
343.93	35.11	14.70	2.457	111.99	13.917
Series II		15.85	2.271	120.25	15.232
7.81	2.6	16.97	2.127	128.58	16.526
8.47	3.9	18.31	1.989	137.08	17.81
8.87	5.9	20.14	1.848	146.07	19.11
9.18	7.9	22.28	1.755	155.56	20.42
9.41	9.2	24.45	1.723	165.25	21.70
9.76	6.5	26.74	1.749	175.00	22.90
		29.39	1.848	184.94	24.06
		32.55	2.045		

Figure 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 II. 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% down to 25°K increasing to 1% at 10°K. The probable error may be 10% 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 Figure 2. Solid lines represent deviations of $\pm 0.1\%$ and $\pm 1.0\%$ respectively. Below 5°K, a Debye third power extrapolation was used to obtain values of the thermodynamic functions. The probable errors in the entropy, enthalpy, and free energy function are estimated to be 0.1% 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.

IV. 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 presented 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 ($S_{298.16}^{\circ} - S_{51}^{\circ}$) are in close agreement. Below 51°K, the extrapolated portion

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TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF ZINC FERRITE

T, °K.	C_p cal/deg	S^0 cal/deg	$(H^0 - H_0^0)$ cal	$-(F^0 - H_0^0)/T$ 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	6.82	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

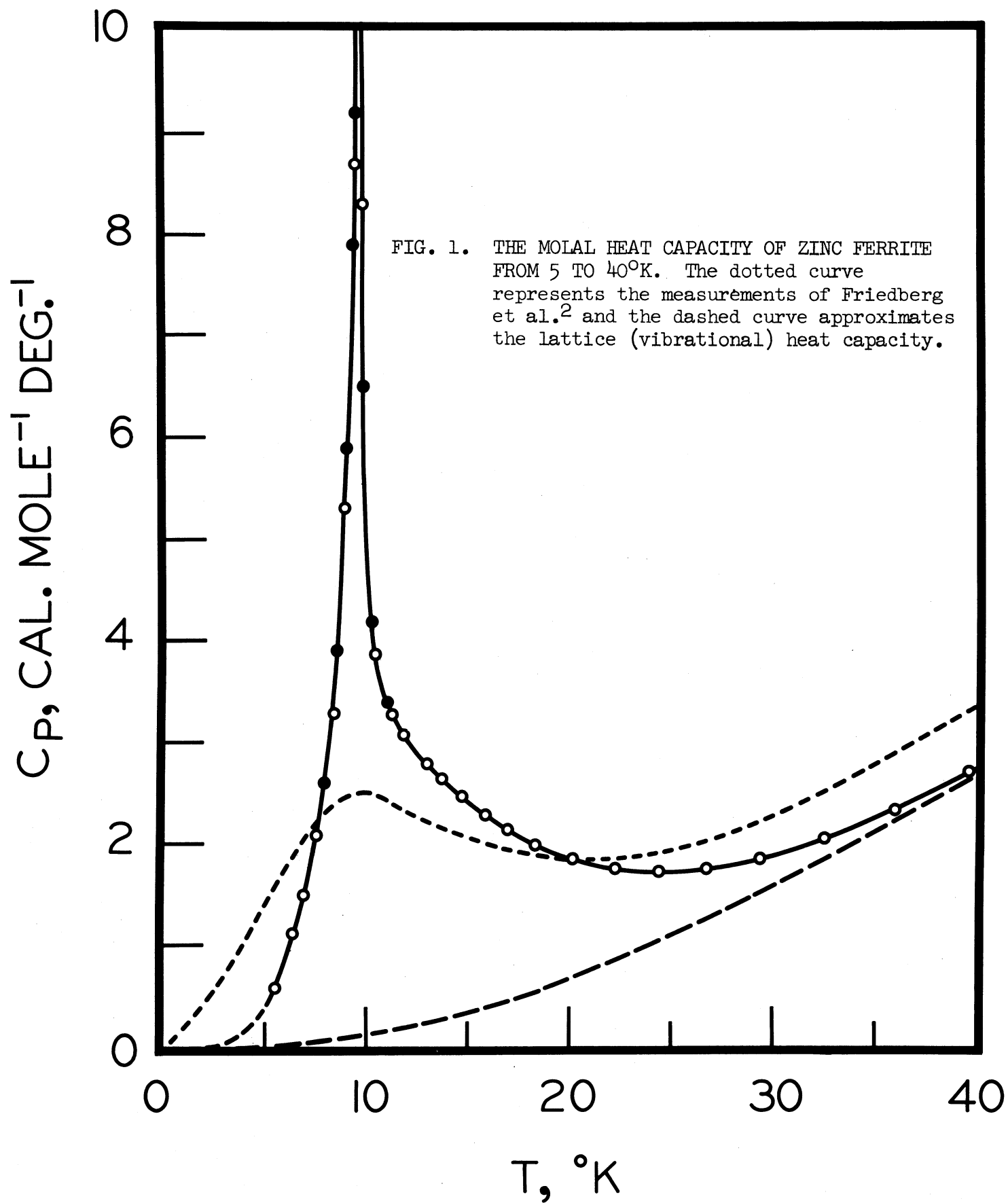
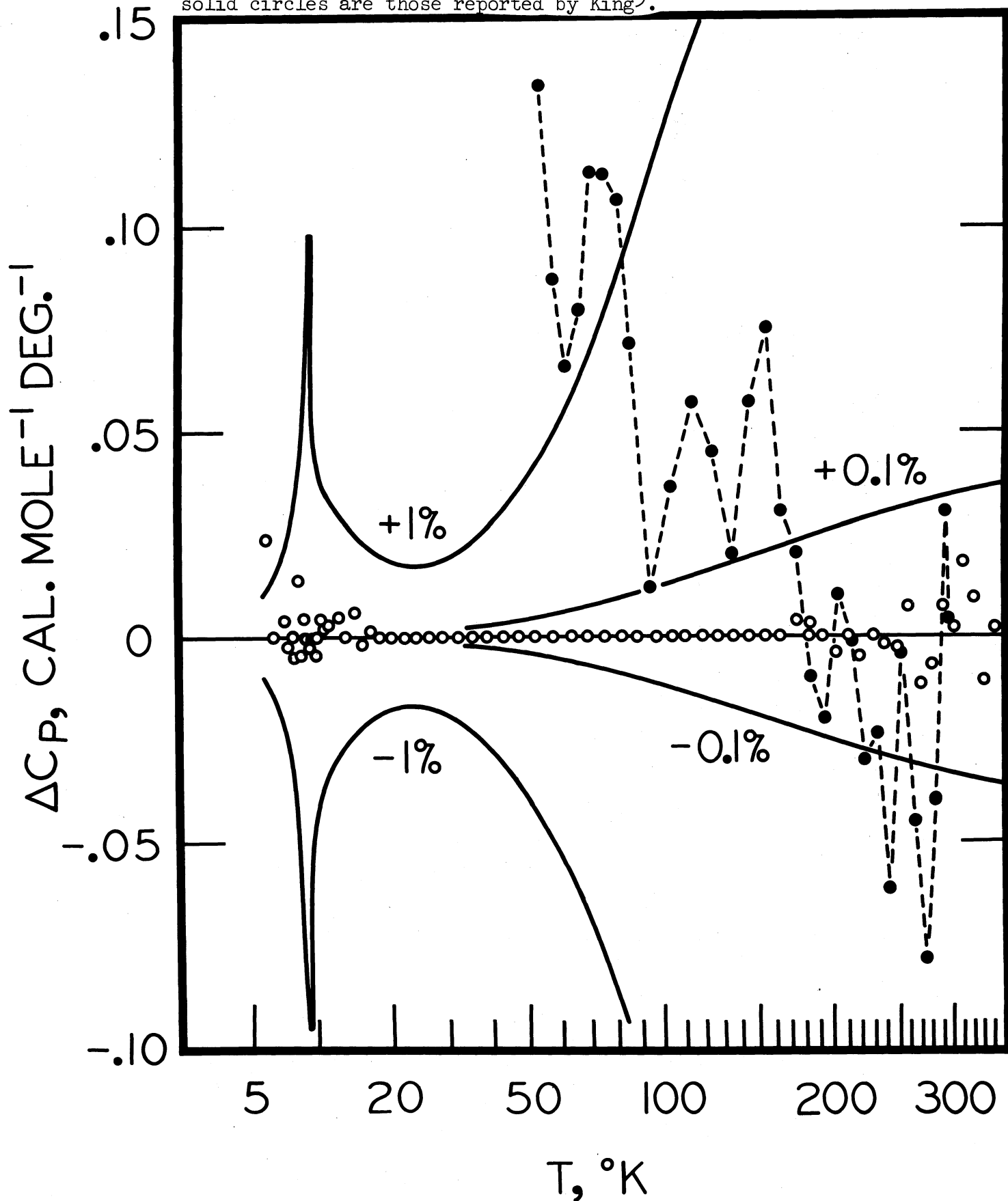


FIG. 2. THE DEVIATION OF THE MEASURES HEAT CAPACITIES OF ZINC FERRITE FROM SMOOTH CURVE, i.e., $\Delta C_p = C_p(\text{exp't'l. det'n.}) - C_p(\text{curve})$. The open circles represent the individual experimental determinations of this work. The solid circles are those reported by King⁹.



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% higher than those reported either in the present work or by King.

The existence of a typical cooperative type heat capacity anomaly rising to a sharp maximum greater than 9 cal mole⁻¹ deg⁻¹ 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 III and indicate good accord with the heat capacity measured with small temperature increments.

Table III

Comparison of Measured and Integrated
Enthalpy Increments

T _{initial} , °K.	T _{final} , °K.	ΔH _{measured}	ΔH _{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

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

Although it is not yet possible to satisfactorily 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 King⁹ 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% 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⁻¹ deg⁻¹ 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 $2 R \ln (S + 1) = 7.12$ (cal./mole deg). The discrepancy between the theoretical value and our rough estimate of the magnetic contribution can readily be resolved 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 Corliss³ of the transition from paramagnetic zinc ferrite to an

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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.

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REFERENCES

1. Grimes, D. M. and Westrum, E. F., Jr., (Submitted to *J. Phys. Chem.*).
2. Friedberg, S. A., et al., "Investigation of Thermal and Electrical Properties of Solids at Very Low Temperature," Carnegie Institute of Technology Report (1955).
3. Hastings, J.M. and Corliss, L. M., *Phys. Rev.*, 102, 1460 (1956).
4. Friedberg, S. A. and Burk, D. L., "Low Temperature Heat Capacity of Some Normal Spinels," Conference on Magnetism and Magnetic Materials, Published by A. Inst. Elec. Engrs., New York, (1955).
5. Westrum, E. F., Jr., and Beale, A. F., Jr., *J. Am. Chem. Soc.* (Submitted).
6. Benjamins, E., and Westrum, E. F., Jr., *J. Am. Chem. Soc.* 00, 0000 (1956) (In press).
7. Hoge, H. H. and Brickwedde, F. G., *J. Research Natl. Bur. Standards*, 22, 351 (1939).
8. Osborne, Stimson, Sligh and Cragoe, *Bur. Standards Sci. Papers*, 20, 65, (1925).
9. King, E. G., *J. Phys. Chem.*, 60, 410 (1956).
10. Westrum, E. F., Jr., and Grimes, D. M., (To be published).
11. Kelley, K. K., Contributions to the Data on Theoretical Metallurgy XI. U. S. Bureau of Mines Bulletin 477. Washington, D. C. (1950).

APPENDIX

The accompanying Tables I through IV list the smoothed values of the heat capacities at selected temperatures of nickel-zinc ferros spinels ($\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$) with $x = 0.6, 0.7, 0.8$ and 0.9 , and the values of the thermodynamic functions computed by numerical quadrature of the heat capacities. For the reasons noted in the paper, the zero-point entropies of these materials are unknown and the entropy increments rather than the entropies are tabulated.

The estimated probable errors of the entropy increments are ± 0.06 e.u. and those of the enthalpy increment are $\pm 0.1\%$. This precision index includes both the uncertainties in the extrapolation and in the measurements themselves.

Molecular weights of 238.404 g., 239.073 g., 239.742 g. and 240.411 g. are taken for $x = 0.6, 0.7, 0.8$ and 0.9 . The data are presented in terms of the defined thermochemical calorie equal to 4.1840 absolute joules and an ice point of -273.15°K .

Table V presents the heat capacity of Ferramic E, a commercial ferros spinel produced by General Ceramic and Steatite Corporation. Measurements were made by the technique described in the paper that this document supplements on a 203.454 g. sample of this material fragmented to 4 to 10 mesh. Calorimeter W-5 was used with Lubriseal grease for thermal conductivity and 760 cm. He at 25°C . to improve the thermal contact with the sample.

The specific heat of this material (in calories $\text{g}^{-1} \text{deg}^{-1}$) represents the fundamental presentation of these data. In addition, primarily for comparison with the other nickel-zinc ferros spinels, the molal heat capacity of this material has been calculated on the assumption that its formula is $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ corresponding to the formula weight 238.404 g. This assumption is consistent with, but not established by, the limiting chemical analysis presented in Table I.

TABLE A.1

MOLAL THERMODYNAMIC FUNCTIONS OF $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$

T, K.	C_p cal.deg. ⁻¹	$S^\circ - S^\circ_0$ cal.deg. ⁻¹	$H^\circ - H^\circ_0$ cal.	$(H^\circ - H^\circ_0)/T$ cal.deg. ⁻¹
10	.232	.077	.58	.058
15	.390	.197	2.09	.139
20	.613	.338	4.57	.229
25	.934	.507	8.39	.336
30	1.367	.714	14.10	.470
35	1.923	.965	22.28	.636
40	2.573	1.263	33.49	.837
45	3.298	1.607	48.14	1.070
50	4.091	1.995	66.59	1.332
60	5.757	2.891	115.96	1.933
70	7.507	3.910	182.31	2.604
80	9.321	5.031	266.40	3.330
90	11.15	6.235	368.76	4.097
100	12.92	7.501	489.11	4.891
110	14.67	8.814	627.0	5.700
120	16.40	10.165	782.4	6.520
130	18.07	11.544	954.8	7.345
140	19.68	12.943	1143.6	8.168
150	21.21	14.353	1348.0	8.987
160	22.67	15.769	1567.5	9.797
170	24.05	17.186	1801.1	10.595
180	25.34	18.597	2048.1	11.378
190	26.55	20.000	2307.6	12.145
200	27.70	21.392	2579.0	12.895
210	28.79	22.769	2861.5	13.626
220	29.79	24.131	3154.4	14.338
230	30.74	25.477	3457.1	15.031
240	31.62	26.804	3768.9	15.704
250	32.46	28.111	4089.4	16.358
260	33.26	29.400	4418.0	16.992
270	34.02	30.669	4754.5	17.609
280	34.74	31.920	5098.3	18.208
290	35.42	33.151	5449.1	18.790
300	36.04	34.362	5806.5	19.355
273.16	34.25	31.067	4862.3	17.800
298.16	35.95	34.140	5740.3	19.252

TABLE A.II

MOLAL THERMODYNAMIC FUNCTIONS OF $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$

T, K.	C_s cal.deg. ⁻¹	$S^0 - S_0^0$ cal.deg. ⁻¹	$H^0 - H_0^0$ cal.	$(H^0 - H_0^0)/T$ cal.deg. ⁻¹
10	.470	.156	1.504	.150
15	.700	.388	4.40	.293
20	.974	.626	8.57	.428
25	1.339	.880	14.30	.572
30	1.812	1.165	22.14	.738
35	2.408	1.487	32.64	.933
40	3.079	1.853	46.35	1.159
45	3.820	2.257	63.56	1.413
50	4.618	2.701	84.65	1.693
60	6.308	3.691	139.20	2.320
70	8.039	4.794	210.97	3.014
80	9.791	5.980	300.05	3.751
90	11.57	7.237	406.9	4.521
100	13.28	8.544	531.2	5.312
110	14.99	9.890	672.5	6.114
120	16.66	11.266	830.6	6.922
130	18.28	12.664	1005.4	7.734
140	19.83	14.075	1195.9	8.542
150	21.32	15.494	1401.7	9.345
160	22.73	16.916	1622.0	10.137
170	24.07	18.334	1856.0	10.918
180	25.31	19.746	2102.9	11.683
190	26.49	21.145	2362.0	12.432
200	27.61	22.533	2632.6	13.163
210	28.66	23.906	2914.0	13.876
220	29.63	25.262	3205.5	14.570
230	30.56	26.600	3506.4	15.245
240	31.44	27.920	3816.4	15.902
250	32.27	29.219	4135.0	16.540
260	33.03	30.499	4461.5	17.160
270	33.74	31.760	4795.4	17.761
280	34.41	32.999	5136.2	18.344
290	35.04	34.218	5483.5	18.909
300	35.64	35.416	5837.0	19.457
273.16	33.96	32.154	4902.4	17.947
298.16	35.53	35.196	5771.5	19.357

TABLE A. III

MOLAL THERMODYNAMIC FUNCTIONS OF $\text{Ni}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$

T, K.	C_s cal.deg. ⁻¹	$S^{\circ}-S_0^{\circ}$ cal. deg. ⁻¹	$H^{\circ}-H_0^{\circ}$ cal.	$(H^{\circ}-H_0^{\circ})/T$ cal.deg. ⁻¹
10	.848	.196	2.877	.288
15	1.057	.574	7.580	.505
20	1.316	.913	13.49	.675
25	1.667	1.243	20.92	.837
30	2.132	1.586	30.35	1.012
35	2.723	1.957	42.45	1.213
40	3.399	2.365	57.74	1.443
45	4.130	2.807	76.54	1.701
50	4.924	3.283	99.16	1.983
60	6.586	4.327	156.69	2.611
70	8.294	5.470	231.06	3.301
80	10.04	6.689	322.63	4.033
90	11.76	7.971	431.60	4.796
100	13.47	9.298	557.7	5.577
110	15.11	10.659	700.7	6.370
120	16.72	12.043	859.8	7.165
130	18.31	13.445	1035.0	7.962
140	19.83	14.857	1225.7	8.755
150	21.28	16.275	1431.4	9.543
160	22.65	17.693	1651.1	10.320
170	23.93	19.106	1884.1	11.083
180	25.15	20.509	2129.6	11.831
190	26.30	21.899	2386.9	12.563
200	27.37	23.275	2655.3	13.276
210	28.37	24.636	2934.0	13.971
220	29.28	25.977	3222.4	14.647
230	30.15	27.299	3519.6	15.302
240	30.98	28.599	3825.2	15.938
250	31.76	29.879	4139.0	16.556
260	32.48	31.138	4460.2	17.155
270	33.14	32.377	4788.3	17.734
280	33.75	33.594	5122.8	18.296
290	34.32	34.788	5463.2	18.839
300	34.83	35.960	5809.0	19.363
273.16	33.33	32.764	4893.3	17.914
298.16	34.74	35.746	5745.0	19.268

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TABLE A.IV

MOLAL THERMODYNAMIC FUNCTIONS OF $\text{Ni}_{0.1}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$

T, K.	C_s cal.deg. ⁻¹	$S^0 - S_0^0$ cal.deg. ⁻¹	$H^0 - H_0^0$ cal.	$(H^0 - H_0^0)/T$ cal.deg. ⁻¹
10	1.747	.737	5.42	.542
15	1.694	1.419	13.84	.922
20	1.752	1.912	22.42	1.121
25	1.956	2.322	31.63	1.265
30	2.317	2.708	42.24	1.408
35	2.827	3.102	55.06	1.573
40	3.444	3.519	70.69	1.767
45	4.136	3.964	89.62	1.991
50	4.885	4.438	112.15	2.243
60	6.470	5.467	168.82	2.814
70	8.101	6.588	241.73	3.453
80	9.773	7.778	331.04	4.138
90	11.45	9.026	437.2	4.858
100	13.08	10.317	559.8	5.598
110	14.69	11.639	698.7	6.352
120	16.28	12.986	853.6	7.113
130	17.84	14.352	1024.3	7.879
140	19.31	15.728	1210.1	8.643
150	20.73	17.108	1410.3	9.402
160	22.07	18.490	1624.3	10.152
170	23.32	19.866	1851.3	10.890
180	24.51	21.233	2090.5	11.614
190	25.63	22.587	2341.2	12.322
200	26.67	23.929	2602.8	13.014
210	27.65	25.255	2874.4	13.687
220	28.54	26.562	3155.3	14.342
230	29.40	27.850	3445.1	14.979
240	30.20	29.119	3743.1	15.596
250	30.95	30.366	4048.9	16.195
260	31.64	31.593	4361.8	16.776
270	32.28	32.799	4681.4	17.338
280	32.88	33.985	5007.2	17.883
290	33.44	35.148	5338.8	18.410
300	33.97	36.291	5675.9	18.920
273.16	32.47	33.177	4783.7	17.512
298.16	33.88	36.082	5613.5	18.827

TABLE A.V

HEAT CAPACITY OF FERRAMIC E

T °K.	Spec. Heat cal. mg. ⁻¹ deg. ⁻¹	C _p cal. mole ⁻¹ deg. ⁻¹	T °K	Spec. Heat cal. gm. ⁻¹ deg. ⁻¹	C _p cal. mole ⁻¹ deg. ⁻¹
Series I			63.00	0.02673	6.373
			69.23	0.03125	7.450
5.59	0.000364	0.087	75.89	0.03621	8.632
6.36	0.000404	0.096	83.03	0.04164	9.927
7.38	0.000564	0.134	90.35	0.04723	11.26
8.65	0.000816	0.195	97.86	0.05281	12.59
10.00	0.001074	0.256	105.87	0.05868	13.99
11.45	0.001292	0.308	114.12	0.06472	15.43
12.94	0.001501	0.358	122.47	0.07068	16.85
14.46	0.001755	0.419	131.20	0.07676	18.30
16.04	0.002051	0.489	140.13	0.08276	19.73
17.72	0.002350	0.561	149.01	0.08851	21.10
19.54	0.002739	0.653	158.03	0.09404	22.42
			167.25	0.09945	23.71
Series II			168.47	0.10012	23.87
			177.45	0.10507	25.05
16.78	0.002226	0.5309	186.57	0.10981	26.18
18.64	0.002599	0.6198	195.75	0.11434	27.26
20.61	0.003038	0.7243	204.81	0.11858	28.27
22.80	0.003617	0.8624	213.75	0.12248	29.20
25.27	0.004320	1.030	222.67	0.12617	30.08
27.97	0.005277	1.258	231.62	0.12974	30.93
30.95	0.006351	1.514	240.59	0.13309	31.73
34.11	0.008154	1.944	249.57	0.13636	32.51
37.47	0.009773	2.330	258.62	0.13934	33.22
41.26	0.011934	2.845	267.81	0.14224	33.91
45.54	0.01457	3.473	276.99	0.14509	34.59
50.25	0.01768	4.215	286.10	0.14756	35.18
55.23	0.02109	5.028	295.17	0.15016	35.80
52.74	0.01937	4.618	304.24	0.15251	36.36
57.47	0.02267	5.405			

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