intensities depend much on the history of the preparation of the samples. The most reproducible form of γ-Al_2O_3, as judged by X-ray and electron diffraction, was obtained by oxidizing in air thin films of aluminum at about 800°.[7] Similar calculations as for γ-Cr_2O_3 were made for this case and the calculated intensity values are set out in Table IV together with the observed values.

TABLE III

OBSERVED AND CALCULATED INTENSITIES FOR VARIOUS DISTRIBUTIONS OF VACANCIES IN γ-Cr_2O_3

γ-Cr_2O_3, u = 0.383, a = 8.36 Å.

	I, calcd.			
hk	Vacancies in oct. sites	Vacancies in tet. sites	Vacancies randomly distributed	X-Ray intensity (visual impression)
111	4.7	36	11.7	Absent
220	33.8	17	27.7	W
311	100	100	100	VS
222	2.4	8.3	4.0	Absent
400	21.1	43.4	27.4	W
440	55.4	61	57	M

TABLE IV

OBSERVED AND CALCULATED INTENSITIES FOR VARIOUS DISTRIBUTIONS OF VACANCIES IN γ-Al_2O_3

γ-Al_2O_3, a = 7.94 Å., u = 0.383

	I, calcd.			
hkl	Vacancies in oct. sites	Vacancies in tet. sites	Vacancies randomly distributed	X-Ray intensity (visual impression)
111	10.6	45.2	19.4	Absent
220	38.8	17.7	31.9	M
311	108	98	105	VS
222	6.8	1.8	4.8	W
400	62.5	95.1	72.2	MS
331	0.5	1.5	0	Absent
422	16.1	7.1	12.6	W
440	100	100	100	VS

The absence of the 111 reflection is significant and almost rules out the possibility of vacancies in tetrahedral positions. There is a fair over-all agreement between the experimental intensities and those calculated on the assumption of the vacancies predominating at octahedral sites. This may indicate a random distribution of vacancies at octahedral positions. Certainly, the possibility of a statistical vacancy distribution both at octahedral and tetrahedral positions cannot be ruled out in the light of the existing data. However, in view of the known distribution in other defect spinels the tentative formula $Al^{3+}[Al^{3+}_{5/3}\square_{1/3}]O_4^{2-}$ may be assigned to γ-Al_2O_3.

Conclusion

X-Ray, electron diffraction and magnetic data for defect spinel type oxides indicate that the cation vacancies predominate among the octahedral positions. In γ-Fe_2O_3 there is an ordered distribution of the vacancies at octahedral sites probably around the cell center. In γ-Mn_2O_3, γ-Cr_2O_3 and γ-Al_2O_3 the vacancies are randomly distributed among the octahedral positions and an ordered superstructure of vacancies is apparently lacking in these oxides.

The tetragonal symmetry of γ-Mn_2O_3 and Mn_3O_4 is to be attributed to the ability of Mn^{3+} ions at octahedral sites to form dsp^2 empty hybrid square bonds with the overlapping oxygen orbitals, the tetragonal structure being further stabilized as a result of the formation by the Mn^{3+} and Mn^{2+} ions of d^2sp irregular tetrahedral bonds at tetrahedral positions. The ideal axial ratio of c/a = 1.16 seems to be attained when both these bonding mechanisms are operative.

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HEAT CAPACITIES AT LOW TEMPERATURES, ENTROPY AND ENTHALPY INCREMENTS OF FOUR NICKEL–ZINC FERROSPINELS[1]

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Heat capacities from 5° to above 300°K. were determined on synthetic samples of $Ni_{1-x}Zn_xFe_2O_4$ with x = 0.6, 0.7, 0.8 and 0.9 to test a hypothesis of Yafet and Kittel concerning triangular transformations. The normal sigmoid dependence of heat capacity on temperature is modified by ferrimagnetic contributions, and an antiferromagnetic transformation near 10°K. becomes increasingly more pronounced with increasing zinc content. Thermodynamic functions have been evaluated from the data presented.

Spinel minerals are fairly common and include important ores. Synthetic ferrospinels (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 (and thereby permitting a more accurate evaluation of the thermodynamic properties) are available probably only for zinc ferrite ($ZnFe_2O_4$).[2] Heat capacity data above 50°K. have, however, been published for more than twelve others,[3] and measurements on magnetite over the range 1.8 to 4.2°K. recently have been published.[4]

(1) Presented at the Ninth Annual Calorimetry Conference in Schenectady, New York, on September 18, 1954. This work was supported by the U. S. Army Signal Corps through the Engineering Research Institute of the University of Michigan.

(2) E. F. Westrum, Jr., and D. M. Grimes, *Phys. and Chem. of Solids*, in press.

(3) E. G. King, *J. Chem. Phys.*, **60**, 410 (1956). *Cf.* the references to other works contained therein.

(4) J. S. Kouvel, *Phys. Rev.*, **102**, 1489 (1956).

The gross magnetic properties of the ferrospinels have been explained by Néel[5] 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 antiferromagnetic interaction between the moments of the two sublattices gives rise to ferrimagnetism at 0°; however, in zinc ferrite ($ZnFe_2O_4$), 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 Kittel[6] 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 Brochet[7] for mixed nickel–zinc ferrites ($Ni_{1-x}Zn_xFe_2O_4$), Yafet and Kittel[6] predicted the possible existence of such multiple transitions in mixed nickel–zinc ferrites with $x > 0.7$.

Such transitions should be detected readily 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 Kittel.[6] 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 $0.6 \leqslant x \leqslant 1.0$. In conjunction with neutron diffraction data[8] it has been established that this anomaly arises as a consequence of the antiferromagnetic–paramagnetic transition 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.

Preparation and Purity of Samples.—Mixed nickel–zinc ferrites, the composition of which may be represented by the empirical formula $Ni_{1-x}Zn_xFe_2O_4$ 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-g. slugs and fired at 1200° for four hours in air and the temperature then reduced 60°/hr. to about 400° 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°/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.[2] Gravimetric chemical analyses for iron and zinc and spectrochemical analyses were made. Stannous chloride oxidation-reduction 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.)	Iron, % Detected	Theor.	Fe^{++}, %
(0.6)[a]	...	46.9 ± 0.1		0.0 ± 0.1
.6	900	46.8 ± .1	46.84	.0 ± .1
.7	(1200)			.1 ± .1
.8	1200	46.7 ± .1	46.59	.0 ± .1
.9	(1200)			.0 ± .1
1.0[b]	1100	46.24 ± .1	46.33	.0 ± .1

[a] Ferramic E, General Ceramic and Steatite Corp.
[b] Per cent. zinc found = 27.2 ± 0.1 (theoretical, 27.12).

Cryogenic Technique.—The design and adiabatic method of operation of the Mark I cryostat[9] and calorimeters W-5[10] and W-9[11] have been described. A calorimeter was in turn loaded with sample, evacuated and 2 to 4 cm. of gaseous helium added at 25° to aid in the establishment of thermal equilibrium. Lubriseal 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 measurement 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.

Heat Capacity Results.—The experimental heat capacity determinations for the four samples of ferrospinels synthesized in this Laboratory are presented in Table II in chronological sequence so that the temperature increments of the individual runs can be inferred 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 ferrite[2] in order to amplify the small differences between these curves. On both

(5) L. Néel, *Ann. phys.*, **3**, 137 (1948).

(6) Y. Yafet and C. Kittel, *Phys. Rev.*, **87**, 290 (1952).

(7) L. Néel and P. Brochet, *Compt. rend.*, **230**, 280 (1950).

(8) J. M. Hastings and L. M. Corliss, *Phys. Rev.*, **102**, 1460 (1956); *Rev. Mod. Phys.*, **25**, 114 (1953).

(9) E. F. Westrum, Jr., and A. F. Beale, Jr. (to be published).

(10) G. A. Burney and E. F. Westrum, Jr. (to be published).

(11) E. Greenberg and E. F. Westrum, Jr., *J. Am. Chem. Soc.*, **78**, 4526 (1956).

TABLE II

MOLAL HEAT CAPACITIES OF NICKEL ZINC FERROSPINELS

(in cal. degree^{-1} g.-mole^{-1})

$Ni_{0.4}Zn_{0.6}Fe_2O_4$ (mol. wt. = 238.404 g.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		219.59	29.73	10.00	0.2317
		228.65	30.61	11.11	.2569
63.23	6.324	237.58	31.41	12.38	.2950
69.11	7.354	246.56	32.19	13.77	.3415
75.83	8.556	255.62	32.91	15.27	.4018
83.16	9.900	264.65	33.62	16.86	.4653
91.49	11.418	273.70	34.30	18.52	.5393
90.54	11.255	282.71	34.92	20.28	.6274
98.30	12.613	291.70	35.52	22.17	.7363
106.78	14.100	300.83	36.09	24.37	.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	.066	38.67	2.394
155.74	22.06	5.65	.085	42.16	2.879
164.52	23.30	4.75	.070	46.10	3.468
173.47	24.51	5.58	.082	50.74	4.204
182.58	25.65	5.49	.080	55.57	5.003
191.87	26.77	6.66	.105	60.34	5.818
201.18	27.83	7.87	.142	65.57	6.376
210.40	28.83	8.96	.184		

$Ni_{0.3}Zn_{0.7}Fe_2O_4$ (mol. wt. = 239.073 g.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
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	.188
64.43	7.079	309.38	36.16	7.59	.300
70.56	8.133	319.94	36.77	8.56	.376
77.46	9.330			9.47	.444
84.48	10.608	Series II		10.33	.4923
91.47	11.826			11.30	.5186
99.32	13.162	173.08	24.45	12.41	.5713
107.50	14.567	182.60	25.62	13.65	.6353
115.56	15.917	192.25	26.75	15.10	.7055
123.76	17.273	201.97	27.81	16.75	.7946
132.32	18.646	211.82	28.84	18.55	.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 g.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
4.95	0.152	33.87	2.581	156.53	22.17
5.45	.154	37.27	3.023	165.21	23.31
5.94	.269	41.13	3.561	174.01	24.46
6.55	.438	45.42	4.196	182.75	25.48
7.49	.578	49.92	4.913	191.53	26.46
8.70	.721	54.87	5.728	200.38	27.42
9.91	.846	60.66	6.694	209.27	28.30
11.17	.8773	67.19	7.809	210.47	28.41
12.50	.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 g.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
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
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	.543	51.44	5.109	220.43	28.59
6.27	.584	56.87	5.958	230.85	29.48
6.59	.647	61.98	6.800	241.44	30.32
6.98	.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

plots the points indicated represent the individual determinations, and the heat capacities of Ferramic E and zinc ferrite[2] have been included for comparison. The significant features are: (1) the sharp antiferromagnetic–paramagnetic transition in zinc ferrite at about 9.7°K. which obviously persists in the mixed ferrospinels 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 Kittel[6] were observed. The ferrimagnetic contributions to the thermal properties cannot at present be quantitatively resolved from those of the lattice.

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 that in the enthalpy increment is ±0.1%. More extensive tabulation of the temperature dependence of the thermodynamic functions of these four ferrites have been prepared.[12]

(12) Extensive tabulation of the heat capacities, enthalpy and entropy increments and enthalpy function of these four ferrospinels in addition to heat capacity data on Ferramic E have been deposited as Document Number 5113 with the ADI Auxiliary Publications

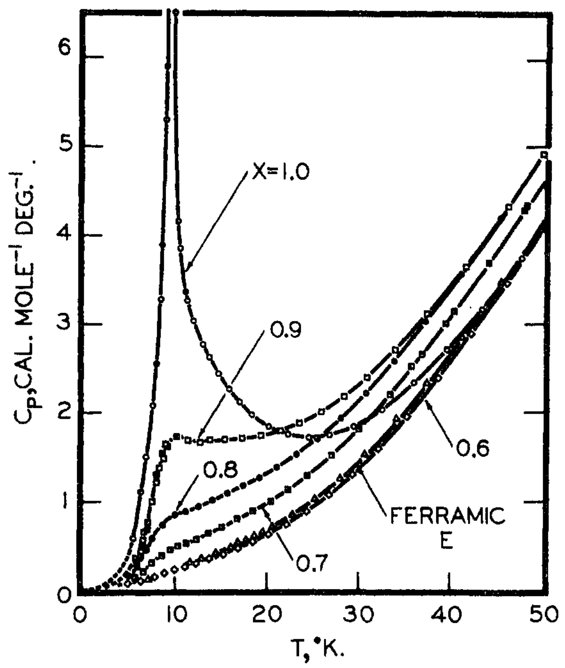

Fig. 1.—Molal heat capacity *vs.* temperature for six samples of $Ni_{1-x}Zn_xFe_2O_4$ compositions below 50°K.

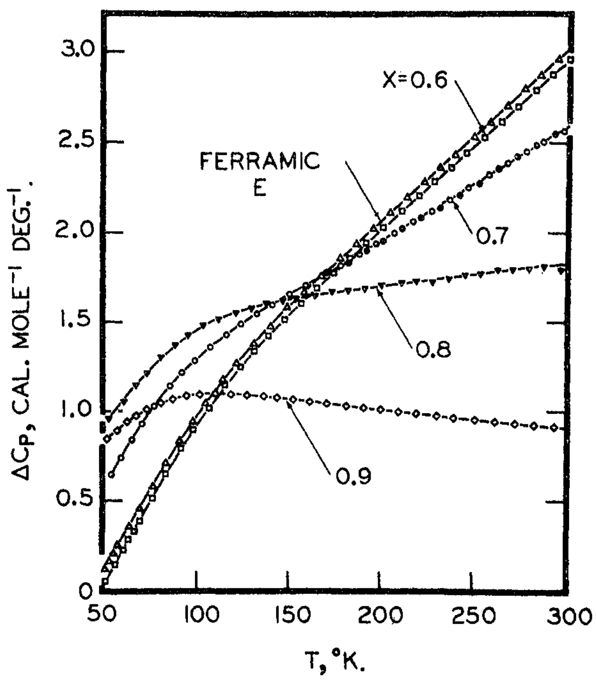

Fig. 2.—Deviation of the experimental molal heat capacity points of $Ni_{1-x}Zn_xFe_2O_4$ from the $ZnFe_2O_4$ smooth curve over the range 50 to 300°K. ($\Delta C_p = C_{p\text{Ferrospinel}} - C_{pZnFe_2O_4}$).

If the nickel ions occupy B sites and zinc ions occupy A sites, then the configurational 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 ions 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 $0.72R$, $1.15R$, $1.46R$ and $1.67R$ 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.

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TABLE III

MOLAL ENTROPY AND ENTHALPY INCREMENTS OF NICKEL–ZINC FERROSPINELS

T, °K.	$x = 0.6$	$x = 0.7$	$x = 0.8$	$x = 0.9$
	$S° - S°_{0i}$ (cal. deg.$^{-1}$ g.-mole^{-1})			
10	0.077	0.156	0.196	0.737
15	.197	.388	0.574	1.419
25	.507	.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
	$H° - H°_0$ (cal. g.-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