

Specific Heat of Pure Zinc and Some Zn-Mn Alloys

DOUGLAS L. MARTIN

Division of Pure Physics, National Research Council of Canada, Ottawa, Canada

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The specific heat of pure zinc and of Zn-Mn alloys containing 0.1 and 0.05 at. % Mn has been measured in the range 0.4 to 30°K. The excess entropy of the alloys, as compared with pure zinc, is about 2.5 cal/°K g atom manganese, indicating a spin of $\frac{3}{2}$ for the Mn atoms. At the lowest temperatures, the specific heat of the more concentrated alloy is linearly proportional to temperature. Above 12°K, the specific heats of both alloys become less than that of pure zinc—possibly a lattice effect due to the light “impurity.” An alloy containing 0.2 at. % Mn was measured in the range 0.4 to 3°K, and below about 0.7°K the specific heat was the same as that of the 0.1-at. % Mn alloy, demonstrating the concentration independence of the limiting low-temperature specific heat. Measurements were also made below 1.5°K on an alloy containing 0.0007 at. % Mn. The superconducting transition temperature was depressed to about 0.5°K, rather lower than expected, and the transition remained of the second order. The variation of electrical resistance with temperature for all the samples was also measured. The temperature of the minimum was proportional to the $\frac{1}{2}$ power of the manganese concentration, in agreement with Kondo’s prediction. A low-temperature maximum in the resistance was observed only for the 0.2-at. % Mn alloy.

1. INTRODUCTION

DILUTE Zn-Mn alloys show¹ the “resistance-minimum” phenomena, indicating localized magnetic moments on the manganese atoms. Other properties of these alloys have been investigated, including magnetic susceptibility,² magnetoresistance,¹ the de Haas-van Alphen effect,³ and specific heat.⁴ The specific-heat measurements⁴ by du Chatenier were on alloys containing 0.07 and 1.5 at. % Mn. Since the maximum solid solubility of manganese in zinc is about 0.5 at. %, it is clear that du Chatenier’s second alloy was not a homogeneous single-phase sample. It follows that conclusions drawn from the measurements by van den Berg⁶ might not have been correct.

In the present work, specific-heat measurements on pure zinc and two dilute alloys have been made in the range 0.4 to 30°K. A third alloy was measured in the range 0.4 to 3.0°K to see whether the limiting low-temperature (linear) specific heat was concentration-independent. In addition, the variation of electrical resistance with temperature of wires made from the specific-heat samples has been measured.

Manganese impurity produces a very rapid depression of the superconducting transition temperature of zinc,⁷ and it was thought worthwhile to measure the specific heat of a very dilute alloy to investigate the detail of the superconducting transition.

2. EXPERIMENTAL

The measurements were made in apparatus which have been described elsewhere,^{8,9} the only change being the use of a germanium rather than a carbon thermometer in the ³He cryostat calorimeter.⁸ Unfortunately, this thermometer, one of two low-resistance thermometers bought from Honeywell, was not completely stable, the calibration altering by several m°K during the course of this work. It was found that the contact resistance of one of the potential leads increased with time and hence the effective length of the germanium in use as a four-terminal resistance probably also varied with time. (The other thermometer open circuited before use.) Furthermore, the calibration between 1.5 and 3°K depended on exchange-gas coupling to a vapor-pressure bulb on the can surrounding the calorimeter. This is not a very satisfactory method owing to unknown temperature gradients. As a result, the present results below 3°K are not as accurate as results obtained more recently on Au-Ag alloys¹⁰ with the same apparatus but using a different thermometer and a much better calibration procedure above 1.5°K. However, preliminary measurements on some of the Au-Ag alloys were made with the Honeywell thermometer and are not significantly different from the later, more precise, results, although much less smooth. As a check on the performance of the calorimeter used in the ³He cryostat for the zinc-alloy measurements, measurements were also made on a pure copper sample consisting of four pieces of $\frac{3}{8}$ -in.-diam ASARCO copper rod in the “as-received” condition. It has since been discovered¹¹ that this material may have a significant specific-heat anomaly in the 1°K region. In the present case, the copper results were quite good ($\gamma = 165.3 \pm 1.1 \mu\text{cal}/^\circ\text{K}^2 \text{ g atom and}$

¹ Y. Muto, Y. Tawara, Y. Shibuya, and T. Fukuroi, *J. Phys. Soc. Japan* **14**, 380 (1959).

² E. W. Collings, F. T. Hedgcock, and Y. Muto, *Phys. Rev.* **134**, A1521 (1964).

³ F. T. Hedgcock and W. B. Muir, *Phys. Rev.* **129**, 2045 (1963).

⁴ F. J. du Chatenier, thesis, University of Leiden, 1964 (unpublished). See also F. J. du Chatenier and J. de Nobel, *Physica* **32**, 1097 (1966).

⁵ M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

⁶ G. J. van den Berg, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. IV, p. 194.

⁷ G. Boato, G. Gallinaro, and C. Rizzuto, *Phys. Rev.* **148**, 353 (1966).

⁸ D. L. Martin, *Proc. Roy. Soc. (London)* **A263**, 378 (1961).

⁹ D. L. Martin, *Phys. Rev.* **141**, 576 (1966).

¹⁰ D. L. Martin (to be published).

¹¹ D. L. Martin, *Rev. Sci. Instr.* **38**, 1738 (1967).

$\theta_0^\circ = 327 \pm 8^\circ\text{K}$ from a least-squares analysis of results from 0.4 to 1.5°K, the error limits being 95% confidence limits), but were not very smooth, deviations from the fitted line being as high as $\pm 2\%$. Therefore, no attempt has been made to smooth the zinc-alloy results on the basis of these "pure" copper measurements. To summarize, the results below 3°K are not as accurate as more recent results from the same apparatus, but since the addition of manganese to zinc produces very large effects in the specific heat at these temperatures, it has not been thought worthwhile to remeasure the samples. The results below 1.5°K should be accurate to $\pm 3\%$ and from 1.5 to 3°K to perhaps $\pm 5\%$. The results above 3°K are estimated to have an accuracy of $\pm 0.5\%$.⁹

Measurements on pure zinc were initially attempted using the copper "tray" technique,⁸ but the silicone grease bond between sample and calorimeter broke on cooling, even when the sample was sawed into a number of pieces to reduce the contact area. (This technique had been satisfactory with cadmium¹² which has a greater over-all contraction from room temperature than does zinc.¹³) Consideration of the limited solid solubility (~ 0.5 at. %) of manganese in zinc suggested that samples with a large ratio of surface area to volume would be advisable so that the whole sample could be cooled quickly on quenching. It was therefore decided that each sample should take the form of four rods about $\frac{1}{2}$ in. in diam and 2 in. long and that the rods would be screwed to the calorimeter. The calorimeters (one for each apparatus) were each made from a single piece of copper in the form of a horizontal cross with a threaded stud ($\frac{1}{2}$ in. long, $\frac{1}{4}$ in. diam, 28 threads per in.) pointing downwards from the end of each arm of the cross. The calorimeter for use in the 3 to 30°K apparatus had a central copper block carrying vapor-pressure bulb, heater, and germanium thermometer. The other calorimeter did not have this block; the heater and thermometer were fitted into holes in the studs.

The pure zinc sample was made from $\frac{1}{2}$ -in.-diam Cominco 69 grade (99.9999% pure) zinc rod. Pieces of about 2 in. length were cut from the rod and a hole was bored and tapped in one end of each piece to fit the studs on the calorimeter. The sample was cleaned after turning but was not heat treated. The total weight of the four pieces was 176.942 g. A semiquantitative spectrographic analysis indicated the following impurities present [all parts per million (ppm) by weight]: Mg < 1, Pb 0.1–5.0, Sn < 0.5, Si 0.01–5.0, Fe 0.05–1.0, Cu < 0.05, Ag < 0.1. Not detected were Ni (< 0.2), Cr (< 1.0), Co (< 0.5), Mn (< 0.2), V (< 0.5), Mo (< 0.2). The rods were screwed to the calorimeter and one satisfactory experiment was made. On cooling a second

time the thermal contact between the rods and calorimeter was unsatisfactory. This difficulty was overcome by applying a small amount (0.01 cc in all) of silicone grease to the threads and this procedure was followed with the Zn-Mn samples also. Comparison of the results with and without grease shows that the thermal capacity of the grease is negligible in comparison with that of the samples. Nevertheless, a measured amount of grease was applied with a hypodermic syringe each time the sample was changed.

The Zn-Mn alloys were made from Cominco 69 grade zinc pellets and "highest-purity electrolytic flakes" of manganese which had been hydrogen treated at 950°C for 3 h and then powdered. Attempts were made to make the Zn-Mn alloys by chill casting, using induction heating under high vacuum. This method was not satisfactory, because of the combined effects of the high vapor pressure of the zinc and the high melting point of manganese. Experience with other alloys containing manganese showed that manganese often interacted with quartz at high temperatures. The alloys were therefore prepared in the following way. For each alloy, a concentrated alloy was first made by heating the components to 700°C for 65 h in an alumina crucible sealed in a quartz tube under a helium/hydrogen atmosphere. In this way, the manganese was dissolved. The required additional amount of zinc was then added to the concentrated alloy ingot and the mixture was heated in a sealed evacuated quartz tube to 550°C for 20 min, well shaken, and quenched in iced water. The quartz tubes did not break, and the alloys were essentially chill cast to the required $\frac{1}{2}$ in. diam. After machining, the samples were placed in sealed Pyrex glass tubes in a helium atmosphere. The 0.05-at. % Mn alloy was heated and held at 395°C for 90 h to homogenize and then quenched in brine (at -15°C) in an attempt to prevent precipitation of the manganese. The 0.1-at. % Mn alloy was held at 390°C for 22 h before quenching and the 0.2-at. % Mn alloy was held at 390°C for 97 h before quenching; in both cases the quenching bath was as above. In all cases the Pyrex glass tubes shattered on quenching, ensuring a rapid cooling of the alloy samples.

[The importance of homogenizing and quenching a chill-cast sample should be noted. In casting a relatively large sample, the last part to be poured may not solidify instantly (evidence for this being a small "pipe" and larger crystals in this region), and hence there may be concentration gradients. Furthermore, a sample quenched from below the melting point can be cooled more quickly than the molten material because there is no latent heat to dissipate. There is also evidence¹⁴ that "clustering" of the minor component may be a function of quenching rate.]

Strips were rolled from pieces taken from each end of the sample rods, cleaned in 50% hydrochloric acid,

¹² D. L. Martin, Proc. Phys. Soc. (London) 78, 1482 (1961).

¹³ R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. (U. S.), Monograph 29 (1961).

¹⁴ R. Tournier, J. J. Veysie, and L. Weil, J. Phys. Radium 23, 672 (1962).

TABLE I. Smoothed results from 3 to 30°K.^a

Temp. (°K)	Pure zinc ^b	Specific-heat cal/°K g atom ($J=4.186$)				Θ^e (°K)
		Pure zinc	Zn-0.1 at. % Mn	Zn-0.05 at. % Mn	Pure zinc rerun	
3	0.000871	0.000867	0.001657	0.001138	0.000852	315.4
4	0.001650	0.001650	0.002350	0.001885	0.001649	307.1
5	0.002992	0.002992	0.003633	0.003205	0.002996	297.2
6	0.005267	0.005258	0.005862	0.005465	0.005268	285.2
7	0.009006	0.008998	0.009578	0.009209	0.009034	272.1
8	0.01496	0.01496	0.01550	0.01517	0.01503	258.9
9	0.02400	0.02399	0.02448	0.02420	0.02410	246.6
10	0.03692	0.03692	0.03732	0.03710	0.03707	236.0
11	0.05435	0.05436	0.05461	0.05445	0.05455	227.3
12	0.07673	0.07673	0.07671	0.07665	0.07691	220.5
13	0.1034	0.1042	0.1039	0.1040	0.1044	215.3
14	0.1371	0.1371	0.1363	0.1365	0.1371	211.4
15	0.1753	0.1752	0.1742	0.1745	0.1752	208.4
16	0.2188	0.2186	0.2173	0.2177	0.2187	206.2
17	0.2671	0.2669	0.2653	0.2659	0.2670	204.7
18	0.3198	0.3196	0.3176	0.3183	0.3196	203.7
19	0.3762	0.3760	0.3737	0.3745	0.3760	203.3
20	0.4359	0.4358	0.4330	0.4341	0.4356	203.1
21	0.4988	0.4987	0.4957	0.4970	0.4987	203.3
22	0.5652	0.5649	0.5618	0.5632	0.5650	203.5
23	0.6347	0.6341	0.6309	0.6322	0.6343	203.9
24	0.7061	0.7057	0.7022	0.7036	0.7058	204.3
25	0.7786	0.7786	0.7748	0.7764	0.7786	204.9
26	0.8527	0.8524	0.8485	0.8503	0.8525	205.7
27	0.9294	0.9278	0.9239	0.9259	0.9280	206.4
28	1.004	1.006	1.002	1.003	1.005	207.1
29	1.078	1.081	1.078	1.079	1.081	208.0
30	1.299	1.146	1.142	1.142	1.143	209.8

^a Atomic weights used: zinc, 65.37; manganese, 54.9381.^b No grease on calorimeter.

distilled water and methanol, and sealed in Pyrex glass tubes in a helium atmosphere. They were then annealed for about 24 h at 390°C and quenched in brine at about -14°C. The resistance ratio $R_{4.2^\circ\text{K}}/R_{293^\circ\text{K}}$ of these strips was as follows: 0.334 and 0.317 for the alloy containing 0.2 at. % Mn, 0.172 and 0.177 for the alloy containing 0.1 at. % Mn, and 0.090 and 0.097 for the alloy containing 0.05 at. % Mn. The alloys were therefore fairly homogeneous and these resistance ratios are in agreement with those obtained by Hedgcock and Muir.³ Also, it does appear that most, if not all, of the manganese in the more concentrated samples is in solution.

The weights of the calorimeter samples were as

TABLE II. Smoothed results from 0.4 to 1.5°K.^a

Temperature (°K)	Pure zinc	Specific-heat $\mu\text{cal}/^\circ\text{K g atom}$ ($J=4.186$)			
		Zn-0.0007 at. % Mn	Zn-0.05 at. % Mn	Zn-0.1 at. % Mn	Zn-0.2 at. % Mn
0.4	...	87	319	351	351
0.5	105	95	373	440	440
0.6	165	95	424	529	529
0.7	214	112	472	616	620
0.8	210	129	514	696	718
0.9	146	146	550	764	815
1.0	165	165	577	824	910
1.1	184	184	596	880	1000
1.2	205	205	604	933	1092
1.3	228	228	612	982	1194
1.4	249	249	622	1031	1302
1.5	274	274	635	1077	1405

^a Accuracy estimated as $\pm 3\%$ (see text).

follows: 177.531 g for the alloy containing 0.05 at. % Mn, 204.207 g for the 0.1% alloy, and 196.149 g for the 0.2% alloy. Two pieces of the last-mentioned alloy were analysed spectrographically and the following impurities were detected (ppm): Mn 300-3000, Mg 0.01-0.1, Pb 0.03-3.0, Si 0.1-1.0, Fe 0.1-1.0, Cu 0.03-1.0.

The alloy containing 0.0007 at. % Mn was made by heating the components to 700°C for 2 h in an evacuated sealed quartz tube. The sample was quenched from the liquid in iced water to chill-cast into the required $\frac{1}{2}$ in. diam. After machining, the sample was heat treated and quenched in the same way as the more concentrated samples. Semiquantitative spectrographic analysis of samples taken from both ends of the cast rod indicated the following impurities to be present (all ppm by weight): Mn (deliberate contamination) 0.5-50, Mg 0.003-0.3, Pb 0.1-3.0, Si 0.01-0.1, Fe 0.03-0.3, Cu 0.3-3.0, Ag 0.03-0.3, Ca 0.03-0.3. The calorimeter sample weighed 194.161 g.

TABLE III. Smoothed results 1.5 to 3.0°K.^a

Temperature (°K)	Specific-heat $\mu\text{cal}/^\circ\text{K g atom}$ ($J=4.186$)			
	Pure zinc ^b	Zn-0.05 at. % Mn	Zn-0.1 at. % Mn	Zn-0.2 at. % Mn
1.6	306	656	1117	1506
1.8	362	693	1193	1695
2.0	424	740	1265	1870
2.2	494	800	1335	2030
2.4	572	870	1405	2170
2.6	659	947	1480	2305
2.8	760	1038	1565	2440

^a These values are based on results of rather poor estimated accuracy between 1.5 and 3.0°K and therefore depend to a large extent on an interpolation between those given in Tables I and II (see text).^b These values are calculated from the extrapolated Θ^e values.

The variation of resistance with temperature of the strips taken from the alloys was investigated by winding each strip on a nylon former. Two formers at a time could be sealed in a copper can containing helium. The can was placed in thermal contact with a copper-"tray"-type calorimeter for measurements in both 3-30°K and 0.4-4.0°K regions. The measurements were made by a potentiometric method using a current of 1 mA. For measurements on the Zn-0.0007-at. % Mn alloy a Keithley model 148 nanovoltmeter was used as detector. For the other alloys a Leeds and Northrup microvolt amplifier was used.

3. RESULTS

In general, two sets of specific-heat measurements were made on each sample, over every part of the temperature range, the apparatus being warmed to room temperature between sets. The sets are distinguished by different symbols in the diagrams which follow.

Smoothed results from the 3-30°K apparatus, obtained by an orthogonal polynomial technique, are

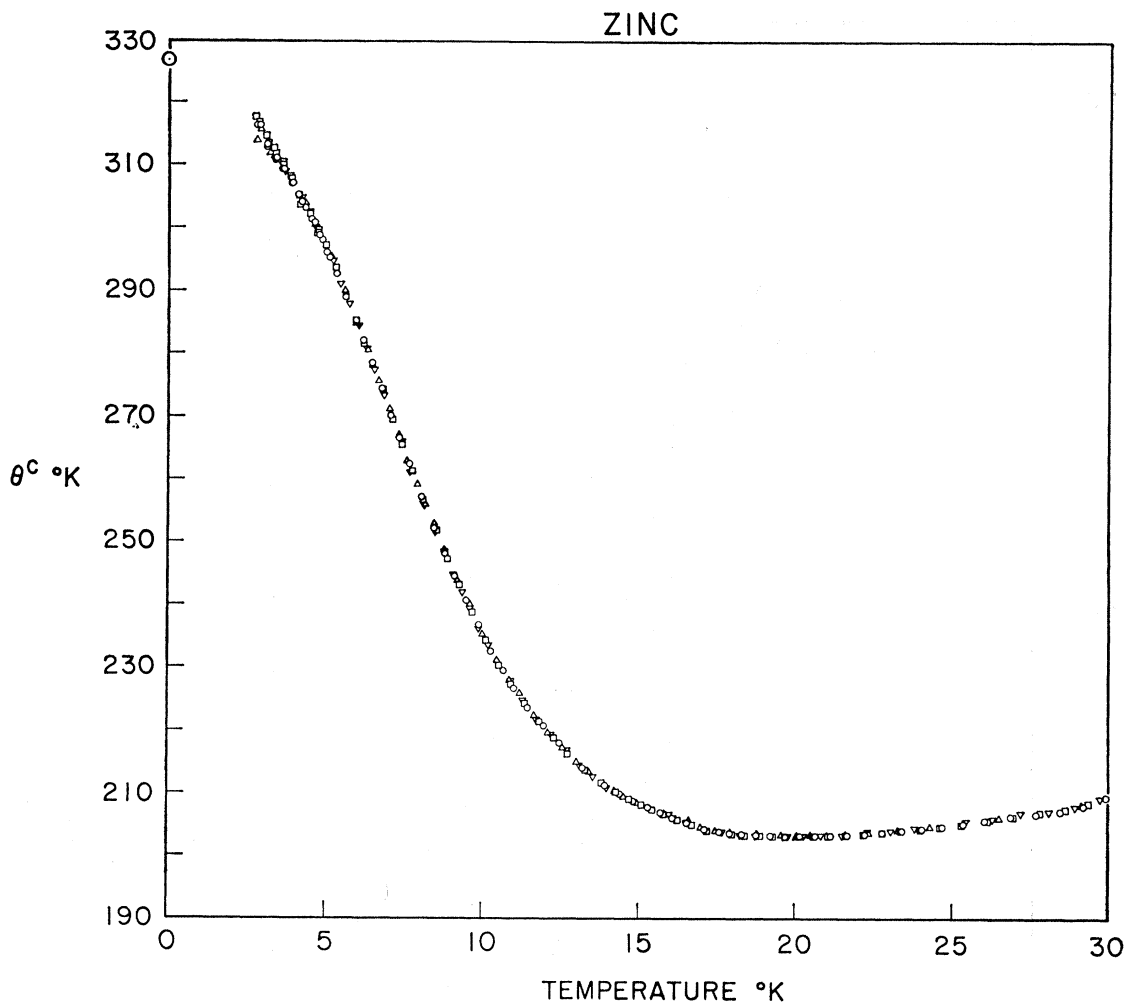


FIG. 1. Plot of Debye temperature Θ° for pure zinc. The point at 0°K is calculated from low-temperature elastic constants.

given in Table I. The Debye temperature Θ° was obtained using the value of $156 \mu\text{cal}/^\circ\text{K}^2 \text{ g atom}$ for the electronic-specific-heat coefficient γ given by Garland and Silverman.¹⁵ Figure 1 shows the raw data for pure zinc in the form of a plot of Debye temperature. Figure 2 shows the differences between the specific heats of the alloys and pure zinc.

Results from the helium-3 cryostat are given in Fig. 3 and in Table II (graphically smoothed results). Owing to the use of a superconducting heat switch, the upper temperature limit for reasonably accurate measurements with this apparatus has been 1.5°K . Also, there was no provision for accurate thermometer calibration above this temperature (see above). This leaves a gap between the measurement ranges of the two apparatuses and this has been filled by less accurate measurements. To measure the empty calorimeter in the $1.5\text{--}3^\circ\text{K}$ temperature range it was necessary to

remove the heat-switch wire and cool with exchange gas. The results of these measurements are given in Fig. 4 and Table III. Figure 5 shows results obtained for the alloy containing $0.0007 \text{ at. } \%$ Mn together with those for pure zinc.

The results of the electrical resistance measurements are given in Figs. 6 and 7. As mentioned earlier, two samples were measured at the same time, the pairs being as follows: 0.05 and $0.2 \text{ at. } \%$ Mn, 0.05 and $0.1 \text{ at. } \%$ Mn, and the two samples of the $0.0007\text{-at. } \%$ Mn alloy.

4. DISCUSSION

Barron and Munn¹⁶ have shown that the present results for pure zinc between 3 and 8°K can be fitted, within 0.2% , by the expression

$$C = (1.56 \times 10^{-4})T + (1.33 \times 10^{-5})T^3 + (1.53 \times 10^{-7})T^5 + (0.92 \times 10^{-9})T^7.$$

¹⁵ C. W. Garland and J. Silverman, *J. Chem. Phys.* **34**, 781 (1961).

¹⁶ T. H. K. Barron and R. W. Munn, *Phil. Mag.* **15**, 85 (1967).

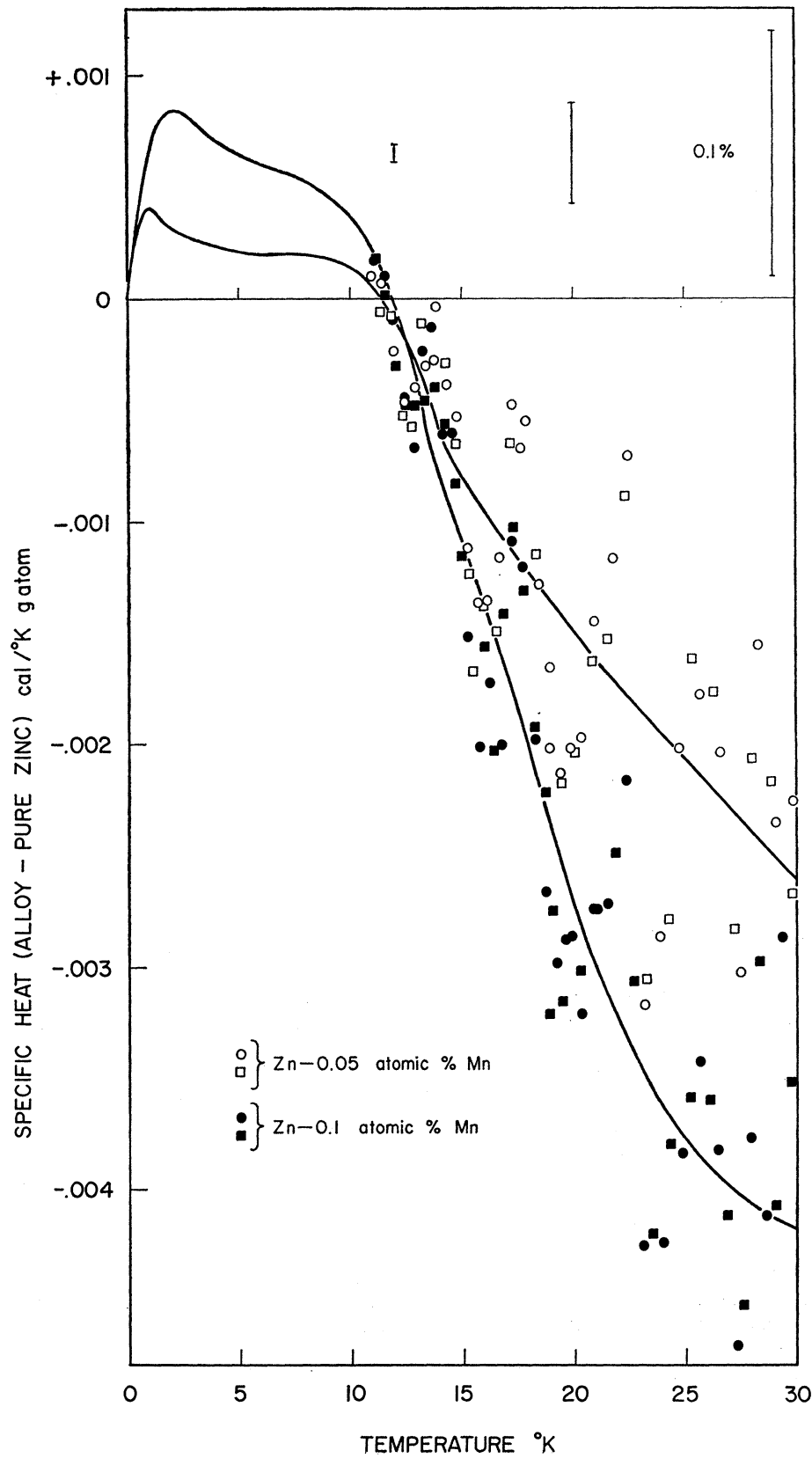


FIG. 2. The difference between the specific heat of the alloys and that of pure zinc in the 3 to 30°K range. The vertical bars indicate 0.1% of the specific heat of pure zinc. (See Fig. 8 for detail below 12°K.)

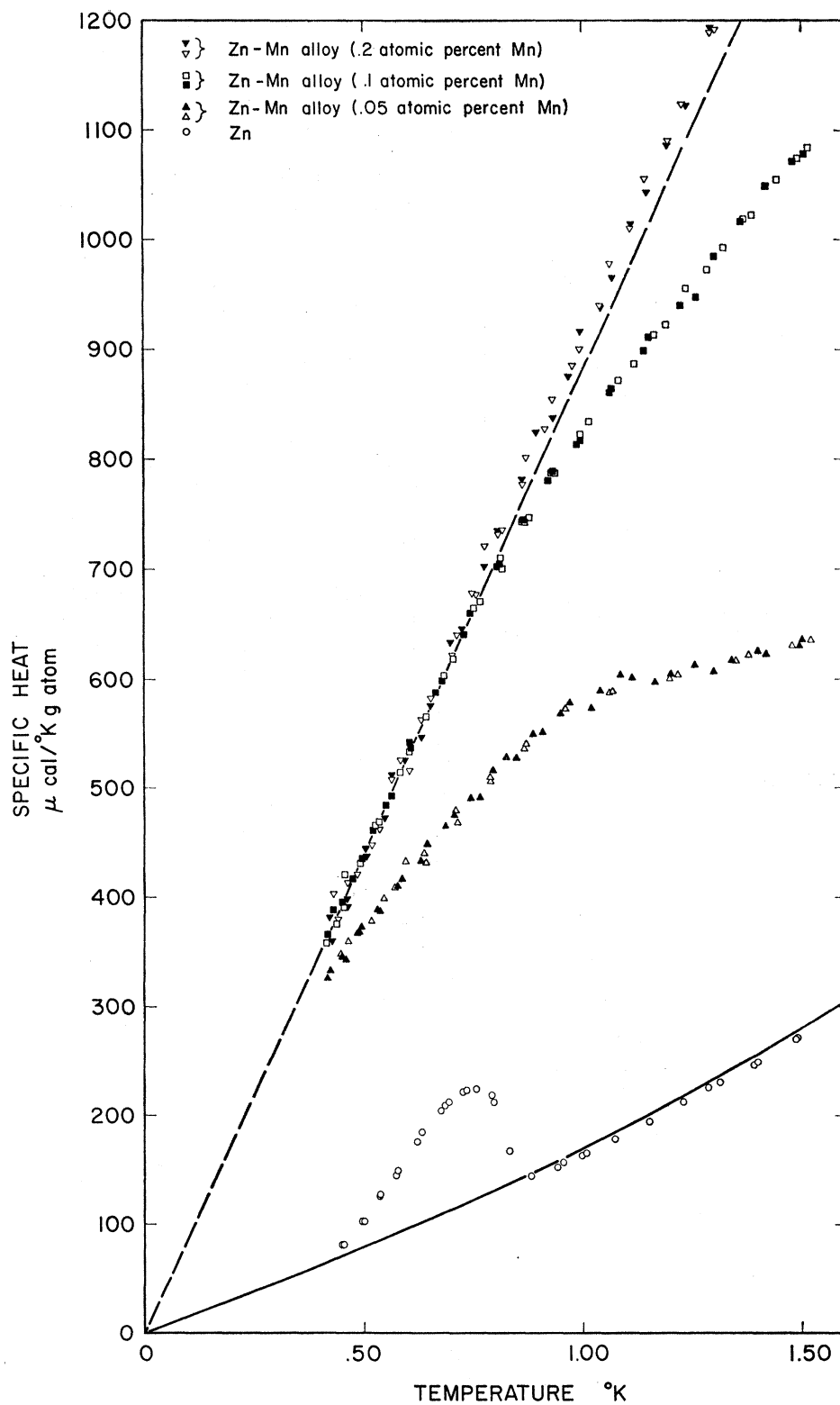


FIG. 3. Specific-heat results below 1.5°K.

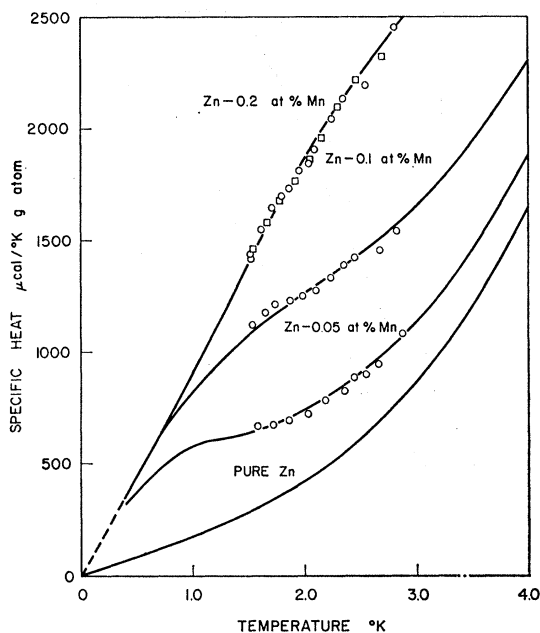


FIG. 4. Specific-heat results in the 1.5–3°K temperature range. These results are less accurate than in the other temperature ranges.

The first term contains the electronic-specific-heat coefficient suggested by Garland and Silverman¹⁵ after a critical examination of data at very low temperatures. The second term corresponds to a limiting Debye temperature Θ_0° of 327°K, in exact agreement with the value Θ_0^{el} deduced from elastic-constant results.¹⁵ The results in the 4–30°K range differ considerably from previous work on zinc (for references see Garland and Silverman).¹⁵

The results for pure zinc obtained with the helium-3 cryostat show a broad superconducting transition, similar to that observed by Seidel and Keesom.¹⁷ In the present case the width might be due to cold-working since the sample was not annealed after machining and in any case there is a differential contraction between the zinc sample and copper supporting screw which would strain the sample on cooling.^{17a} The present results for the normal state lie about 3% below the value expected from an extrapolation of the higher-temperature results to the Θ_0^{el} value. This may be indicative of the accuracy of the results below 3°K.

Examination of Fig. 2 shows that above about 12°K the specific heat of the alloys is slightly less (about 0.5% maximum difference) than that of pure zinc. The small

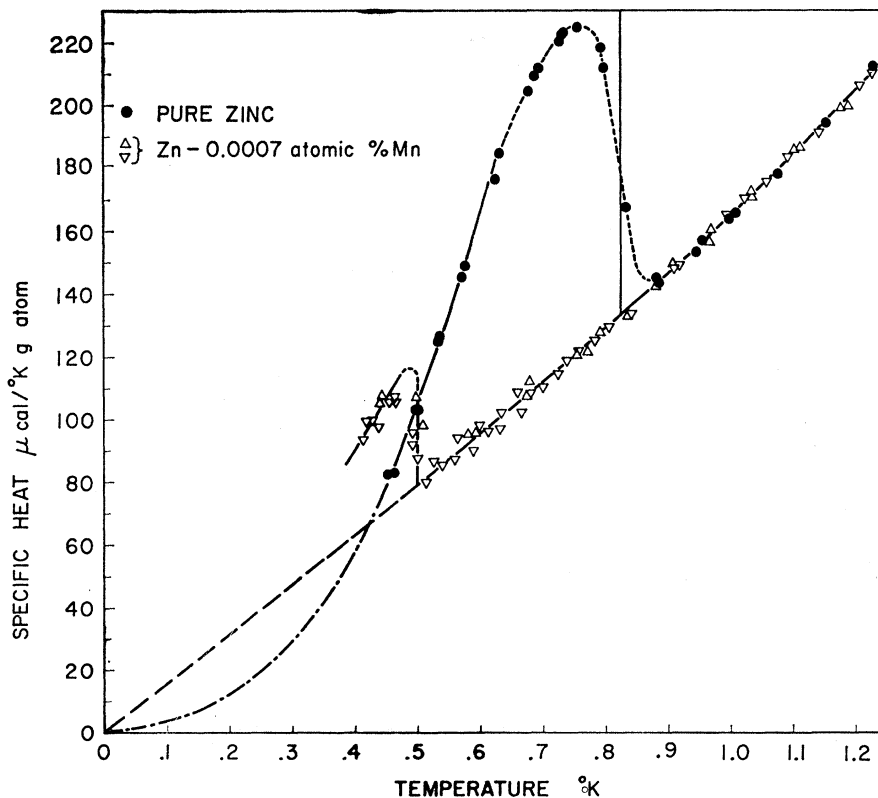


FIG. 5. Specific heat of pure zinc and a Zn-0.0007-at. % Mn alloy.

¹⁷ G. Seidel and P. H. Keesom, Phys. Rev. **112**, 1083 (1958).

^{17a} Note added in proof. R. E. Fassnacht and J. R. Dillinger [Phys. Rev. **164**, 565 (1967)] have observed that the superconducting transition in zinc is broadened in magnetic fields of less than 0.3 Oe. They believe that this effect is related to the condition of the surface of the sample and is not accounted for by strain or impurities.

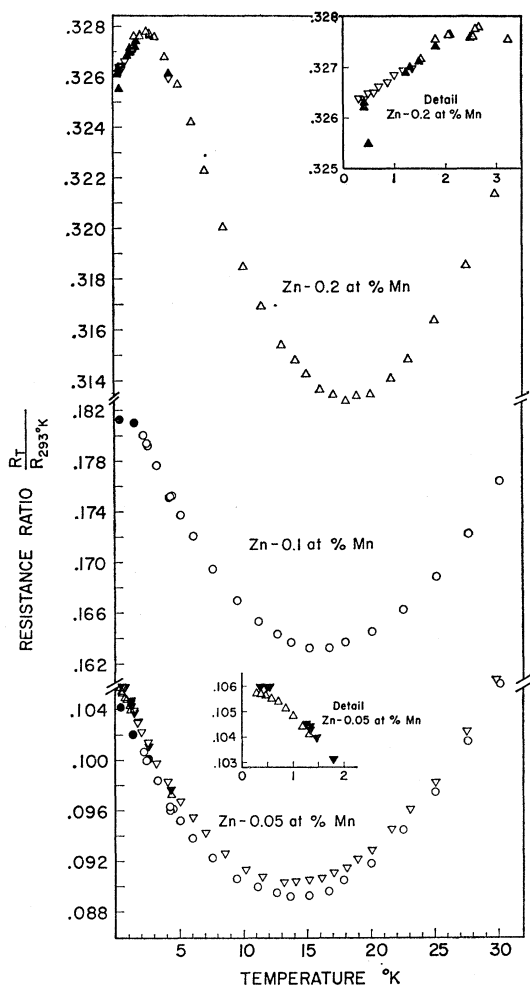


FIG. 6. Electrical resistance ratio versus temperature for the more concentrated Zn-Mn alloys.

difference was confirmed by remeasuring pure zinc after the alloy measurements, closely confirming the original measurements on pure zinc (see Table I). It is possible that this difference is due to the lighter "impurity" manganese atoms producing high-frequency "impurity" modes in the lattice vibration spectrum with consequent depletion of some lower-frequency part of the vibration spectrum.¹⁸ (The converse effect in more concentrated alloys has been reported recently.¹⁹)

The effect discussed in the previous paragraph makes it difficult to obtain the exact shape of the anomaly associated with the magnetic ordering of the manganese atoms. It will be assumed that the lattice and electronic specific heats of the alloys are the same as those of pure zinc. Figure 8 shows these anomalies as a plot of the excess specific heat ΔC_p versus temperature and Fig. 9 gives the same information in the form of a plot

¹⁸ P. Dean, Proc. Roy. Soc. (London) A260, 263 (1961).

¹⁹ H. Culbert and R. P. Huebener, Phys. Letters 24A, 530 (1967). Reference to other similar work will be found in this paper.

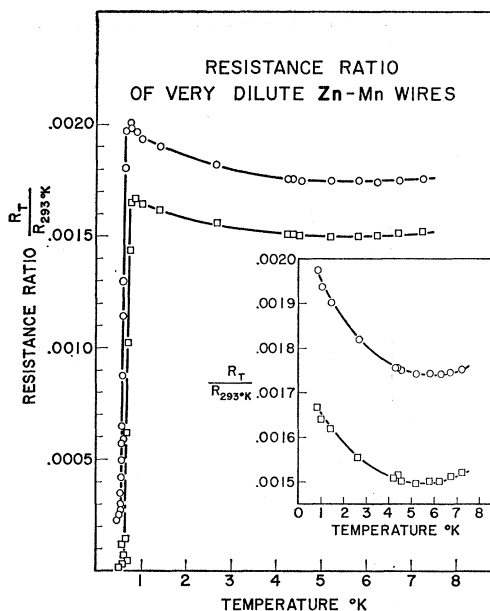


FIG. 7. Electrical resistance ratio versus temperature for two samples from the Zn-0.0007-at. % Mn alloy.

of $\Delta C_p/T$ versus temperature. The area under the curve in this plot is the entropy associated with the anomaly and this is 0.00236 cal/°K g atom for the 0.1-at. % alloy and 0.00124 cal/°K g atom for the 0.05-at. % alloy. These figures are respectively equivalent to 2.4 and 2.5 cal/°K g atom manganese and are accurate to about 5%. However, they should be regarded as lower limits because of the fact that the lattice specific heat of the alloys is probably slightly less than that of pure zinc, as discussed above. If the spin S is taken as $\frac{3}{2}$ then $R \ln(1+2S)$ is 2.77 cal/°K g atom and if $S=1$, $R \ln(1+2S)$ is 2.2 cal/°K g atom. Thus the spin on the manganese ion is probably $\frac{3}{2}$, a value previously deduced from magnetic-susceptibility results.²

It is clear from Fig. 3 that the 0.2- and 0.1-at. % alloys show a concentration-independent linear term in the specific heat at the lowest temperatures. The 0.05-at. % alloy is obviously tending towards this same linear specific heat. The coefficient of this term is about 880 $\mu\text{cal}/^\circ\text{K}^2$ g atom, corresponding to an excess over pure zinc of 720 $\mu\text{cal}/^\circ\text{K}^2$ g atom. Some time ago, both Overhauser²⁰ and Marshall²¹ were able to account for this linear term in terms of static spin-density waves and the Rudermann-Kittel-Yosida interaction, respectively. More recently, Kondo²² has suggested that the term is simply an enhanced electronic specific heat as a

²⁰ A. W. Overhauser, Phys. Rev. Letters 3, 414 (1959); J. Phys. Chem. Solids 13, 71 (1960). Later work [L. L. van Zandt and A. W. Overhauser, Phys. Rev. 141, 583 (1966)] has shown that a consistent interpretation of the observed transport anomalies may not be possible on the static spin-density-wave hypothesis. See also Gonser *et al.* (Ref. 42).

²¹ W. Marshall, Phys. Rev. 118, 1519 (1960).

²² J. Kondo, Progr. Theoret. Phys. (Kyoto) 33, 575 (1965).

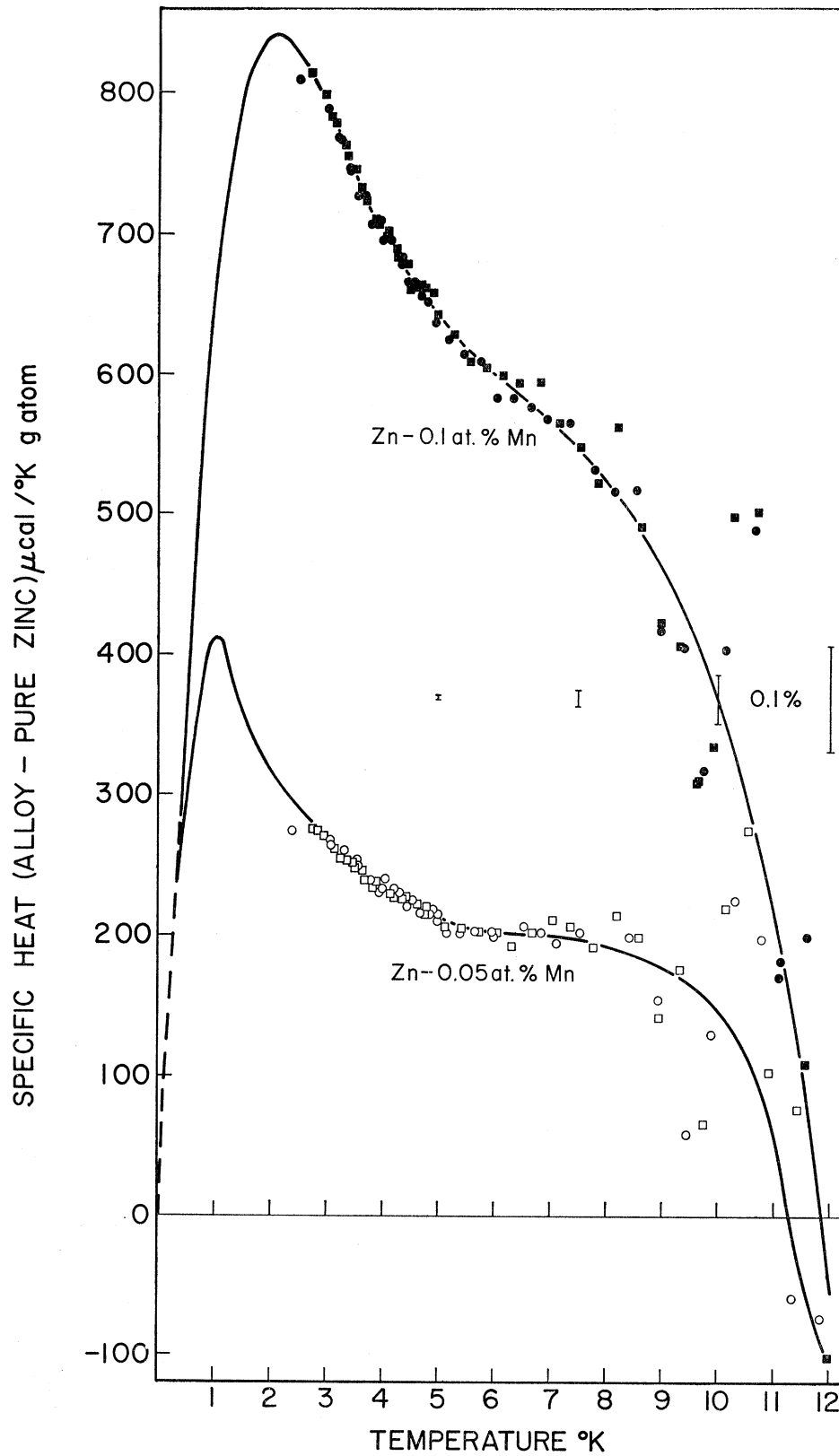


FIG. 8. Plot of "excess" specific heat versus temperature for the alloys.

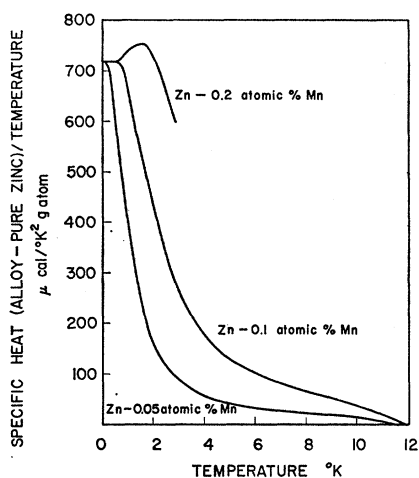


FIG. 9. Plot of ("excess" specific heat)/temperature versus temperature for the alloys.

result of electron-spin-electron interactions. Klein²³ claims that a more exact calculation of this (Kondo) effect gives a term of the form $(-T \ln T)$ and states that in any case Kondo's approximate result could not account for more than a third of the observed effect. Klein maintains that most or all of the linear term is accounted for by magnetic disordering.²⁴ The local minimum at $H=0$ in the probability distribution of the total field, predicted by Klein,²⁴ is confirmed by the results of a Mössbauer experiment.²⁵ Assuming that the whole of the linear specific-heat term is accounted for by Klein's theory it is possible to compare values for JS^2 for different alloys (where J is the interaction energy between the impurity spins of magnitude S) since the linear "magnetic" specific-heat term is inversely proportional to this quantity. Some data are listed in Table IV. It will be observed that all reported linear terms are of the same order of magnitude. Most comparisons in the literature²⁴ have been with Cu-Mn since a great deal of information on the magnetic and other properties of this system is available. It is important to note that the most recent results on this alloy, at temperatures below 1°K,²⁶ have given a linear term considerably smaller than was obtained at higher temperatures.²⁷ Very recently it has been suggested²⁸ that the effective ferromagnetic exchange interaction between conduction electrons, produced by the presence of magnetic impurities, will increase the electronic specific heat by a spin-fluctuation mechanism. There

²³ M. W. Klein, Phys. Rev. Letters **16**, 127 (1966).

²⁴ M. W. Klein, Phys. Rev. **136**, A1156 (1964).

²⁵ W. Marshall, T. E. Cranshaw, C. E. Johnson, and M. S. Ridout, Rev. Mod. Phys. **36**, 399 (1964).

²⁶ F. J. du Chatenier and A. R. Miedema, Physica **32**, 403 (1966); J. C. Ho [thesis, University of California, Berkeley, 1965 (unpublished)] has suggested that the analysis of these results is incorrect and hence the linear terms are incorrect.

²⁷ L. T. Crane and J. E. Zimmerman, J. Phys. Chem. Solids **21**, 310 (1961).

²⁸ D. J. Kim and B. B. Schwartz, Phys. Letters **24A**, 77 (1967).

TABLE IV. Coefficients of excess specific heat, linear in temperature, at low temperatures, $\mu\text{cal}/^\circ\text{K}^2 \text{g atom}$.

Alloy	Coefficient
Zn-Mn ^a	720
Mg-Mn ^b	1900
Cu-Mn ^c	900
Cu-Mn ^d	560
Cu-Fe ^e	560
Au-Mn ^d	1860
Au-Fe ^d	540
Ag-Mn ^d	1100
Cu-Cr ^d	430

^a This work.

^b D. L. Martin, Can. J. Phys. **39**, 1385 (1961).

^c Crane and Zimmerman (Ref. 27).

^d du Chatenier and Miedema (Ref. 26).

^e J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

has also been recent criticism²⁹ of the earlier theories. The most recent paper³⁰ concludes that "the mechanism of the observed (specific-heat) anomalies must remain an open question."^{30a} At the present time it would be charitable to suppose that several different mechanisms may be contributing toward the specific-heat anomalies.

The results for the 0.2-at. % Mn alloy suggest that the shape of initial part of the specific-heat anomaly tends to curve upward rather than downward (as in the case for the more dilute alloys). This variation of shape with concentration has been predicted by Liu³¹ but he also found that an upward curvature would be associated with a smaller linear term in the specific-heat anomaly. This is not the case for the alloy range studied in the present work.

Measurements on the alloy containing 0.0007-at. % manganese were made in order to investigate the effect on the superconducting transition. It is known⁷ that Mn produces a very rapid depression of the transition temperature of zinc and 7 ppm (at.) Mn was expected⁷ to depress the temperature by about 0.22°K. The present results suggest a depression rather greater than 0.3°K and it does seem unlikely that the alloy contained considerably more than the stated amount of manganese. The reverse might be expected since there is a possible loss due to oxidation³² and reaction with the container during melting. The sharpness of the observed transition (see Fig. 5) suggests that the alloy was rather homogeneous and the general shape of the curve indicates that the transition remains of the second

²⁹ S. Nakajima, Phys. Letters **24A**, 33 (1967).

³⁰ D. R. Hamann, Phys. Rev. **158**, 570 (1967).

^{30a} Note added in proof. An even more recent paper is P. E. Bloomfield and D. R. Hamann, Phys. Rev. **164**, 856 (1967), where the specific-heat anomaly resulting from correlation between the impurity and conduction-electron spins is obtained. This may be the explanation of the specific-heat anomalies observed in CuFe but does not explain the anomalies observed in ZnMn.

³¹ S. H. Liu [Phys. Rev. **157**, 411 (1967)] has assumed (with some justification) that the most probable value of the effective field decreases with increasing temperature. The Klein-Brout theory leads to the opposite conclusion. This might be because they have only considered correlation between two spins which is not a correct assumption for more concentrated alloys.

³² D. H. Howling, Phys. Rev. **155**, 642 (1967).

order. These results for the transition of a superconductor containing an impurity carrying a localized moment should be compared with previous results³³ for Al-Mn where the impurity is thought to have no localized moment.^{33,34} The general picture is very similar except for the much more rapid depression of transition temperature in the former case.

Theoretical treatments for the depression of superconducting transition temperature in the case of localized moments have been summarized by Boato *et al.*,⁷ and for the case of no localized moments the most recent work is that of Ratto and Blandin.³⁵ Examination of the specific-heat results³³ for Al-0.045-at. % Mn shows that the ratio of the change in specific heat at the superconducting transition temperature for the dilute alloy and pure metal (0.74) is nearly equal to the ratio of the transition temperatures (0.72). (For a recent theoretical treatment of the thermodynamic properties of such alloys see Kiwi and Zuckermann.³⁶) For the Zn-0.0007-at. % Mn alloy the specific-heat ratio³⁷ is about 0.26 while the transition-temperature ratio is 0.61. Theory³⁸ indicates that, in the case of impurities with localized magnetic moments, the specific-heat ratio will decrease more rapidly than the transition-temperature ratio. However, the theoretical result would require a change in specific heat at the transition temperature for the alloy almost twice as great as is suggested by Fig. 5. (The step for the alloy was obtained by extrapolating the solid curves and ignoring the dashed curve.) At present this discrepancy looks real but specific-heat measurements to lower temperatures would be necessary to establish it beyond all doubt. A comparison of results³⁹ for La-Gd alloys with the same theory³⁸ showed agreement within the experimental uncertainties. However, manganese in zinc depresses the superconducting transition temperature about 500 times more rapidly than does gadolinium in lanthanum.

The electrical resistance measurements on strips made from the 0.0007-at. % manganese sample are shown in Fig. 7. The concentration of manganese in these strips is probably lower than that in the sample due to cleaning and possible oxidation³² of the manganese. Even so, there is a clear resistance minimum in both strips and the superconducting transition

temperature is depressed to about 0.7 and 0.6°K, respectively.

The electrical-resistance measurements^{39a} on the more concentrated alloys (Fig. 6) show a well-defined resistance minimum. There is a maximum for the 0.2-at. % alloy. The maximum is well established since it appeared in independent measurements in the two different apparatus. The first set of measurements below 1°K indicated another minimum in resistance but this was not confirmed by a more detailed second set of measurements and it is clear that one point of the first set is in error. The resistance of the 0.1-at. % manganese alloy appears to be reaching a constant value as the temperature is reduced and inspection of the "detail" diagram for the 0.05-at. % manganese alloy shows the same behavior. Measurements below 0.4°K would be necessary to confirm the absence of a low-temperature maximum in the resistance. The temperature of the minima in the resistance plots are rather closely proportional to the ($\frac{1}{2}$) power of the concentration as predicted by Kondo.⁴⁰ Even for the strips made from the 0.0007-at. % Mn alloy the minimum temperature is within a factor of 2 of that predicted from the results for the more concentrated alloys. The perturbation method used by Kondo fails at lower temperatures and a quasi-bound state is gradually formed between the localized spin and conduction-electron spin. A great deal of recent theoretical work has been concerned with this problem and has been summarized by Hamann.³⁰ Harrison and Klein⁴¹ have investigated the variation of resistivity with temperature for the two cases of (i) long-range order and (ii) short-range order via a Rudermann-Kittel-Kasuya-Yosida interaction. The internal fields will quench the Kondo $\ln T$ dependence of resistance at very low temperatures. They conclude that the second alternative is correct and predict that the temperature of the resistance maximum will be proportional to concentration. This is not the case for the alloys which have been investigated in the present work.

At one time⁴² it seemed that these dilute alloys could be divided into two groups depending on whether the electrical resistance as a function of temperature showed only a minimum, apparently saturating at a certain value as the temperature was lowered, or whether the minimum was followed by a maximum as the tempera-

³³ D. L. Martin, Proc. Phys. Soc. (London) **78**, 1489 (1961).

³⁴ E. Daniel and J. Friedel, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press Inc., New York, 1965), p. 933.

³⁵ C. F. Ratto and A. Blandin, Phys. Rev. **156**, 513 (1967).

³⁶ M. Kiwi and M. J. Zuckermann, Phys. Rev. **164**, 548 (1967).

³⁷ N. E. Philips [Phys. Rev. Letters **1**, 363 (1958)] found a sharp superconducting transition in the specific heat of zinc at 0.825°K and his value of the change in specific heat at this transition temperature has been used for pure zinc.

³⁸ S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. **136**, A1500 (1964).

³⁹ D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965).

^{39a} Note added in proof. New electrical resistance measurements on Zn-Mn alloys published recently by F. T. Hedgcock and C. Rizzuto [Phys. Rev. **163**, 517 (1967)] appear to be in substantial agreement with the present results. However, their claimed observation of a resistance maximum in some of the more dilute alloys is not confirmed by the present, more precise, results.

⁴⁰ J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

⁴¹ R. J. Harrison and M. W. Klein, Phys. Rev. **154**, 540 (1967).

⁴² D. L. Martin, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1963), p. 243. See also U. Gonser, R. W. Grant, C. J. Meehan, A. H. Muir, and H. Wiedersich, J. Appl. Phys. **36**, 2124 (1965).

ture was lowered. It will be clear that Zn-Mn alloys may not fall into either of these groups. A good example in the first group of alloys was Cu-Fe, but Svensson⁴³ has recently reported that cold-worked Cu-Fe alloys may show a resistance maximum also. It might be that cold-working has increased the solid solubility of iron in copper or has altered the distribution of iron in the copper. (A similar effect may occur in In-Mn alloys where chill-cast and extruded samples⁴⁴ have a much higher solid solubility than those which are merely quenched.⁴⁵) For a given alloy system there may be a critical concentration below which a resistance maximum does not occur and in alloys of rather limited solid solubility (e.g., Cu-Fe) the likelihood of observing a resistance maximum is reduced. Another recent development is the suggestion by Schrieffer⁴⁶ that the Kondo theory⁴⁰ may explain the occurrence and non-occurrence of localized magnetic moments in dilute solutions of transition metals, i.e., resonant anti-ferromagnetic exchange scattering exactly compensates the spin of the localized moment in some cases. (This approach contrasts with the traditional theory³⁴ which neglects correlation effects between electrons.) Daybell

and Steyert⁴⁷ have followed up Schrieffer's suggestion and have summarized the experimental evidence for the quasi-bound state in very dilute alloys. For more concentrated alloys the picture may be complicated by interaction effects between the transition metal impurities in the temperature region where they show a magnetic moment.

5. CONCLUSION

Below about 12°K Zn-Mn alloys show a large specific-heat anomaly suggesting that the manganese ions in solution have spin $\frac{3}{2}$. A concentration-independent specific heat, linear in temperature, is observed at the lowest temperatures. Above about 12°K the specific heat of the alloys becomes slightly less than that of pure zinc, probably a lattice-specific-heat effect due to "impurity" modes. Measurements on a very dilute alloy show a marked depression of the superconducting transition temperature but the transition remains second order.

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⁴³ K. Svensson, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966* (Proizvodstvenno-Izdatel'skii Kombinat, VINITI, Moscow, USSR, 1967).

⁴⁴ D. L. Martin, *Phys. Rev.* **138**, A464 (1965).

⁴⁵ G. Boato, M. Bugo, and C. Rizzuto, *Nuovo Cimento* **B45**, 226 (1966).

⁴⁶ J. R. Schrieffer, *J. Appl. Phys.* **38**, 1143 (1967).

⁴⁷ M. D. Daybell and W. A. Steyert (to be published).