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# Specific heat of a dilute magnetic alloy with magnetic interactions: ZnMn†

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We have measured the specific heat of pure Zn and of a series of five ZnMn alloys (60, 112, 213, 530, and 1200 ppm Mn) as a function of temperature $T$ from 0.7 to 4 K in zero external magnetic field. The excess specific heat, $\Delta C = C(\text{alloy}) - C(\text{pure Zn})$, is proportional to the square of the Mn concentration $n$ for $T/n > 6 \times 10^{-3}$ K/ppm and $n > 200$ ppm Mn, indicating the presence of magnetic interactions between the Mn impurities in the three most concentrated alloys. We find that $\Delta C$ as measured for the 213, 530, and 1200 ppm alloys also obeys the scaling law of Blandin and Souletie for impurities interacting via a $1/r^3$ Ruderman-Kittel-Kasuya-Yosida (RKKY) potential, $\Delta C/n = f(T/n)$. $\Delta C$ for the 60- and 112-ppm-Mn alloys contains an additional contribution above that due to interactions, presumably the result of single-impurity effects. We propose a simple analytic expression for the excess specific heat due to interacting Mn impurities in Zn, viz., $\Delta C = AT/(1+BT^2/n^2)$. From $\Delta C$ we have derived expressions for the free energy, internal energy, and entropy. In addition to being in good agreement with our experiment results and obeying the scaling laws of Blandin and Souletie, these thermodynamic functions coincide in the high-temperature limit with the predictions of Larkin and Khmel'nitskii for the thermodynamic functions of an alloy with magnetic impurities interacting via RKKY. Comparing theory and experiment for $\Delta C$, we find $S=3/2$ for the spin of the Mn impurity and $V_0=(0.91 \pm 0.01) \times 10^{-36}$ erg cm$^3$ for the strength of the RKKY interaction between two Mn impurities.

## I. INTRODUCTION

At liquid-helium temperatures specific-heat anomalies are observed in many dilute alloys of nontransition metals (such as Cu, Ag, Au, Zn) with transition metal impurities (such as Fe, Cr, Mn).[1] Magnetic measurements at higher temperatures on the same alloys give evidence for well-defined magnetic moments associated with the impurities. Hence the specific-heat anomalies are associated with a magnetic transition in the interacting system of the magnetic impurities and the conduction electrons.

The character of the magnetic transition occurring in a particular alloy system depends critically on the concentration $n$ of magnetic impurities present in the alloy. As the temperature of the alloy is lowered, there are two competing interactions occurring within the magnetic-impurity–conduction-electron system: (i) single-impurity (Kondo) interactions[2] with a characteristic energy $k_BT_K$, where $T_K$ is the Kondo temperature, and (ii) impurity-impurity [Ruderman-Kittel-Kasuya-Yosida (RKKY)] interactions[3] with characteristic energy $nV_0$, where $V_0$ is the strength of the RKKY interaction. At very low $n$, where $nV_0 \ll k_BT_K$, single-impurity effects are usually dominant, and the specific-heat anomaly, which occurs over a wide range of temperatures, has a concentration-independent peak at about $\frac{1}{3}T_K$.[4] The limiting low-$T$ state in this case is thought to be nonmagnetic.[2] For higher concentrations, where $nV_0 > k_BT_K$, interaction effects dominate and the broad specific-heat anomaly has a peak at a temperature proportional to $n$ and of the order of $nV_0/k_B$.[5-7] For $T \ll nV_0/k_B$ a "spin-glass" state is reached in which the impurity spins are strongly correlated with each other, but without long-range magnetic order present.[8] Our approach in this work will be to concentrate on effects due to magnetic interactions between the Mn impurities in Zn.

The spin-glass picture of a random array of interacting magnetic impurities in a nonmagnetic metallic host has provided a useful physical description of the interesting phenomena which such alloy systems display. The onset of short-range (magnetic) order at low temperatures is evidenced by the existence of maxima in both the specific heat and magnetic susceptibility. It is now generally accepted that the exchange forces which couple the magnetic impurities are due to the RKKY interaction,[3] and that the important properties of the spin glass are a consequence of the oscillatory dependence of the interaction on the distance between the impurities. As a result, there is no long-range ordered state at low temperatures, since both ferromagnetic and antiferromagnetic interactions are possible. The $1/r^3$ falloff of RKKY allows "scaling laws" for the specific heat, susceptibility, free energy, etc., to be formulated which indicate that the temperature $T$ at which an anomaly occurs should scale with the concentration $n$ of magnetic impurities.[9,10]

The calculation of the actual dependence of the specific heat, or any other property, on $T$ and $n$ from a physically justifiable model has proven remarkably difficult. At low $T$ the Marshall-Klein-Brout theory[5,6] predicts the observed behavior of the specific heat by using an Ising model for spins which interact via RKKY. The Ising-model approach has recently been criticized because it gives a probability function $P(H_i)$ of local fields $H_i$ with a finite $P(0)$.[8,11,12] In a more realistic three-dimensional model, however, it is expected that $P(0)=0$. It should be mentioned that Klein has recently calculated the specific heat at low $T$ using a Heisenberg model and has found $\Delta C$ proportional to $T$ and independent of $n$.[13] At high $T$ progress has recently been made by Larkin and Khmel'nitskii through the use of a virial expansion of the free energy in a power series of the density of impurities.[7] Their predictions for the free energy and specific heat are in agreement with the scaling laws.

In order to study these effects at low $T$ from measurements of specific heat, it is necessary to examine a series of alloys with $n$ varying over as wide a range as possible. From measurements of $\Delta C$ over a wide range of $n$ and $T$, one then looks for the following characteristic types of behavior: (i) For single-impurity effects, $\Delta C/n$ for an alloy system will be a function only of $T$,[4] and (ii) for RKKY-interaction effects, $\Delta C/n$ for an alloy system will obey a scaling law, i.e., will be a function only of $T/n$.[9,10] No theoretical predictions have yet been made for the case when single-impurity and interaction effects are present in the same alloy.

We have chosen to make specific-heat measurements on a series of dilute ZnMn alloys (60–1200-ppm Mn) for the following reasons: (a) ZnMn with sufficiently dilute concentrations of Mn impurities (0–20- ppm Mn) is a well-characterized Kondo system with $T_K = 0.24$ K and spin $\approx 1.5-2$,[14] and (b) at higher concentrations interaction effects between Mn impurities in Zn have been observed in several properties: magnetic susceptibility,[15] resistivity,[15,16] and specific heat.[17] However, no systematic study of these interactions effects had previously been undertaken, due to the difficulty of separating the contribution of single impurities from that due to the interacting impurities. In addition, there had been a lack of well-defined theoretical predictions for the effect on experimentally observable quantities of the magnetically interacting impurities.

Since the concentration of our most dilute alloy is 60 ppm Mn, we expect that interaction effects will be observed in all our samples. We note that specific-heat measurements for the determination of $\Delta C$ would be very difficult for ZnMn alloys in the range of 0–20 ppm Mn with our present apparatus. We will compare our experimental results for $\Delta C/n$ with the scaling law of Blandin and Souletie, $\Delta C/n = f(T/n)$.[9,10] Also, at low $T/n$ comparison will be made with the predictions of Klein's mean-random-field calculation[6] and at high $T/n$ with the predictions of Larkin and Khmel'nitskii.[7] A preliminary report of this work has been published.[18]

## II. EXPERIMENTAL

### A. Sample preparation

The ZnMn alloys used for these specific-heat measurements were in the form of polycrystalline cylinders (1.3 cm diam by 5 cm long), with masses typically of 50 g. The alloys were prepared from United Mineral Co. Zn (99.9999% purity) and Johnson Matthey Mn (99.99% purity). Initially, a master alloy of Zn + 5000- ppm Mn was cast by melting the constituents under an atmosphere of argon in a Pyrex tube carbon coated with Aqua Dag. The actual alloys studied, in the 60–1200-ppm-Mn range, were prepared by diluting the master alloy to the desired concentration with an appropriate amount of pure Zn. The constituents were then cast into a 1.3-cm-diam carbon-coated Pyrex tube, using an overpressure of argon. The alloys were shaken to ensure good mixing and then were annealed just below their melting point for 4–5 h. After a rapid quench, the samples were allowed to anneal at room temperature for a year before use.

When measurements of specific heat were completed, the concentrations of the alloys were checked by measuring the residual-resistance ratios of thin slabs cut from each end of the cylinder.[19] The concentrations of the alloys were determined to be 60 ± 1, 112 ± 1, 213 ± 10, 530 ± 30, 1200 ± 100 ppm Mn, where the results represent averages of the concentrations determined for the two ends of the sample. These actual concentrations are consistently higher than the nominal concentrations (50, 100, 200, 500, 1000 ppm Mn). Large-concentration gradients (greater than 10%) were observed only in the 1200-ppm-Mn sample, and this is reflected in the measured excess specific heat for this sample, to be discussed later.

### B. Measurement of specific heat

A $He^3$ cryostat was used for the measurement of specific heat of these ZnMn alloys in the range from 0.7 to 4 K. The calorimeter consisted of a brass can which enclosed the sample and which was detachable from the bottom of the $He^3$ chamber. This calorimeter was thermally isolated from the $He^4$ bath by means of a high-vacuum space. The sample space inside the brass can was evacuated and at no time was exchange gas introduced. Thermal contact to the $He^3$ chamber was provided in either of two ways: (i) by pulling the sample holder up against the bottom of the $He^3$ chamber for measurements above 1.5 K, and (ii) by using a Pb superconducting heat switch below 1.5 K.

The sample holder consisted of a Au-plated copper clamp which held the sample firmly and to which a germanium thermometer and constantan heater were attached. The sample holder was suspended by means of a nylon cord, which was part of the mechanical heat switch used above 1.5 K. All electrical leads to the sample holder were thermally shorted at 1.5 and at 0.5 K and consisted of PbSn-solder-plated No. 40 constantan wires to minimize Joule-heating and thermal-conduction effects.

A Solitron germanium thermometer was used for the entire temperature range over which measurements were made. This thermometer had been calibrated against cerium magnesium nitrate (CMN). Two separate least-mean-square fits were used for this thermometer. In the range below $T=1.3$ K, a fit of $1/T$ to a four-term polynomial in $(\ln R)^{1/2}$ was found which reproduced the 38 calibration points with an error for each point no greater than $5\times10^{-4}$ K. Above 1.3 K, a fit of $1/T$ to a five-term polynomial in $R^{1/2}$ was used. The accuracy of the calibration points in this temperature region was only $\pm5\times10^{-3}$ K, due to the relatively small rate of change of resistance of the thermometer. At 4.2 K the resistance of the thermometer was 35 Ω.

Data was recorded automatically as follows: Thermometer voltages and currents and sample heater currents as measured by a Hewlett-Packard 2460A digital voltmeter with a Keithley-140 nV amplifier, and heating-period times as measured by a Hewlett-Packard 5223L electronic counter, were recorded on magnetic tape via a Dymec 2546A magnetic-tape coupler and a Kennedy 1406 magnetic-tape transport.

Discrete heating periods of 19 sec followed by drift periods of 77 sec were used throughout these measurements. Temperature readings taken during the drift periods were least-mean-squares fitted to a quadratic polynomial in time. The temperature-vs-time fits were then extrapolated to the midpoints of the heating periods to determine $\Delta T$, the temperature increase resulting from power $Q$ dissipated in the sample heater. The heat capacity

TABLE I. Smoothed specific-heat results from 0.6 to 4.0 K.[a]

| | Specific heat in mJ/g K | | | | | |
|---|---|---|---|---|---|---|
| $T$ (K) | Pure Zn[b] | Zn+60 ppm Mn | Zn+112 ppm Mn | Zn+213 ppm Mn | Zn+530 ppm Mn | Zn+1200 ppm Mn |
| 0.6 | (0.006 10) | | | 0.0167 | | |
| 0.7 | (0.007 20) | | 0.011 00 | 0.0167 | 0.0321 | 0.0379 |
| 0.8 | (0.008 30) | 0.010 00 | 0.011 60 | 0.0171 | 0.0357 | 0.0432 |
| 0.9 | 0.009 45 | 0.010 95 | 0.012 40 | 0.0175 | 0.0381 | 0.0485 |
| 1.0 | 0.010 70 | 0.012 00 | 0.013 35 | 0.0182 | 0.0399 | 0.0532 |
| 1.1 | 0.011 95 | 0.013 15 | 0.014 40 | 0.0190 | 0.0411 | 0.0576 |
| 1.2 | 0.013 25 | 0.014 40 | 0.015 55 | 0.0199 | 0.0416 | 0.0617 |
| 1.3 | 0.014 60 | 0.015 70 | 0.016 80 | 0.0210 | 0.0421 | 0.0655 |
| 1.4 | 0.016 05 | 0.017 05 | 0.018 15 | 0.0222 | 0.0426 | 0.0692 |
| 1.5 | 0.017 55 | 0.018 55 | 0.019 60 | 0.0234 | 0.0431 | 0.0727 |
| 1.6 | 0.019 15 | 0.020 10 | 0.021 10 | 0.0247 | 0.0437 | 0.0762 |
| 1.7 | 0.020 85 | 0.021 75 | 0.022 75 | 0.0262 | 0.0445 | 0.0798 |
| 1.8 | 0.022 60 | 0.023 45 | 0.024 45 | 0.0277 | 0.0455 | 0.0830 |
| 1.9 | 0.024 50 | 0.025 30 | 0.026 30 | 0.0294 | 0.0468 | 0.0863 |
| 2.0 | 0.026 50 | 0.027 30 | 0.028 20 | 0.0312 | 0.0482 | 0.0897 |
| 2.2 | 0.030 80 | 0.031 55 | 0.032 45 | 0.0351 | 0.0514 | 0.0958 |
| 2.4 | 0.035 65 | 0.036 40 | 0.037 25 | 0.0396 | 0.0554 | 0.1017 |
| 2.6 | 0.041 10 | 0.041 80 | 0.042 60 | 0.0447 | 0.0599 | 0.1073 |
| 2.8 | 0.047 25 | 0.047 90 | 0.048 70 | 0.0506 | 0.0651 | 0.1135 |
| 3.0 | 0.054 15 | 0.054 80 | 0.055 55 | 0.0572 | 0.0711 | 0.1202 |
| 3.2 | 0.061 90 | 0.062 55 | 0.063 25 | 0.0647 | 0.0780 | 0.1279 |
| 3.4 | 0.070 65 | 0.071 25 | 0.071 90 | 0.0732 | 0.0860 | 0.1366 |
| 3.6 | 0.080 45 | 0.081 05 | 0.081 65 | 0.0828 | 0.0952 | 0.1464 |
| 3.8 | 0.091 40 | 0.092 00 | 0.092 55 | 0.0936 | 0.1056 | 0.1574 |
| 4.0 | 0.103 70 | 0.104 30 | 0.104 80 | 0.1056 | 0.1174 | 0.1697 |

[a] The accuracy of these results is estimated to be ±2%. The estimated precision in mJ/g K is as follows: for pure Zn, Zn+60 ppm Mn, and Zn+112 ppm Mn, ±0.00005–±0.0001; for the Zn+213 ppm Mn and Zn+530 ppm Mn, ±0.0001–±0.0002; and for the Zn+1200 ppm Mn, ±0.0005.

[b] The values in parentheses are obtained from an extrapolation of our results above 0.9 K, where Zn is in the normal state.

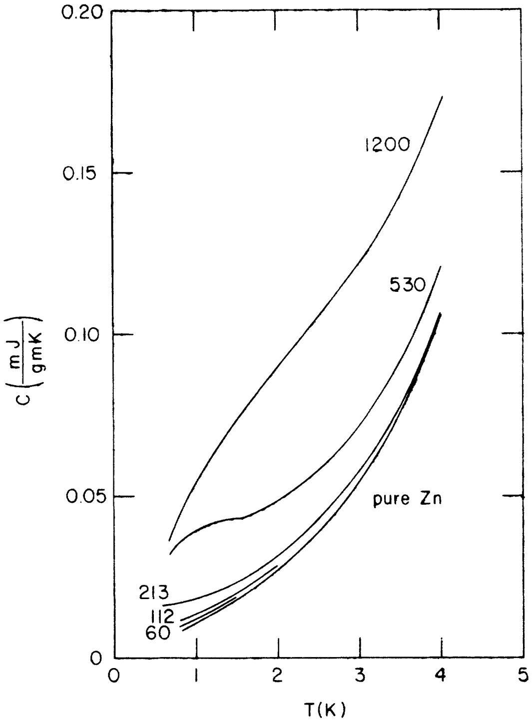

FIG. 1. Smoothed specific-heat results in the range 0.7–4 K. Concentrations are in parts per million Mn.

was then calculated from $Q/\Delta T$. The heat capacity of the sample holder as determined from a separate run was never more than 20% of the total heat capacity.

## III. RESULTS

At least two separate specific-heat measurements were made on pure Zn and each of the five alloys studied here. Computer-smoothed results are given in Table I, and are plotted as a function of temperature in Fig. 1. Above 1.5 K, the data for the 60- and 112-ppm-Mn alloys are not included in Fig. 1, as they fall only slightly above the data for pure Zn. In Fig. 2 results are shown for the excess specific heat per unit Mn concentration, $\Delta C/n$, as a function of temperature.

## IV. DISCUSSION

### A. Pure zinc

We have fitted our results for the specific heat of pure Zn to within ± 2% by the following expression (in units of mJ/g K),

$$C = 9.876\times10^{-3}T + 7.871\times10^{-4}T^3 + 1.348\times10^{-5}T^5 \quad , \tag{1}$$

and have used this expression to calculate the values of $C$ for pure Zn given in Table I and Fig. 1. Our values for pure Zn agree with those of Martin to within 1% below 2 K and, from 2 up to 4 K, are from 1 to 3% lower than his values.[17] For $\gamma$, the coefficient of the linear term in the electronic specific heat, we obtain $9.876\times10^{-3}$ mJ/g K$^2$, which is 1.5% higher than Martin's value, $9.727\times10^{-3}$ mJ/g K$^2$. From the cubic term in Eq. (1), we find a Debye temperature of 335.5 K, which is 2% higher than Martin's value of 329.2 K.

### B. ZnMn alloys

Our search for interactions contributing to the specific heat of ZnMn begins with Fig. 2, where $\Delta C/n$ is shown as a function of $T$. Single-impurity theory predicts that, for a given alloy system, $\Delta C/n$ should be a function of $T$ alone.[4] The existence of interactions between the Mn impurities and their effect on $\Delta C/n$ is clearly evident in Fig. 2, particularly for the three highest concentration alloys, 213, 530, and 1200 ppm Mn, where $\Delta C/n$ is observed to be a function of both $T$ and $n$. We attribute the broad "maximum" in $\Delta C/n$ as a function of $T$ for the 1200-ppm-Mn sample to the previously mentioned concentration gradients in this sample. Consequently, we shall disregard our results for $\Delta C$ above 3 K for this alloy.

To study further the concentration dependence of $\Delta C$, we plot $\Delta C/n$ as a function of $n$ in Fig. 3. At low $n$ we find that $\Delta C/n$ is proportional to $n/T$. However, there is an obvious deviation from this proportionality to $n$ as $n\to 0$. We attribute this behavior to an extra contribution to $\Delta C$ from single-impurity effects at very low concentrations. The $n^2$ dependence of $\Delta C$ at low $n$ suggests that interacting pairs of Mn impurities first contribute to $\Delta C$ as $n$ increases into the range where interactions among the Mn impurities are important. As can be seen from Fig. 3, $\Delta C/n$ versus $n$ reaches a maximum at a value of $n$ which increases proportional to $T$. The decrease of $\Delta C/n$ as $n$ increases further can be understood as the "freezing" in orientation of the impurity spins as interactions increase and the spin-glass state is approached.[8] We note that in this limit, for $n$ large, our results are consistent with $\Delta C/n$ decreasing as $1/n$ so that $\Delta C$ at a given $T$ is independent of $n$.

We summarize our results for $\Delta C$ of ZnMn as displayed in Figs. 2 and 3: (a) $\Delta C$ is initially linear in $T$ and independent of magnetic impurity concentration $n$ at low temperatures; (b) as $T$ increases further, $\Delta C$ goes through a peak whose temperature $T_{\max}$ is proportional to $n$; (c) $\Delta C$ is quadratic in $n$ and inversely proportional to $T$ for $T/n > 6\times10^{-3}$ K/ppm and $n > 200$ ppm. (a) and (b) above have been predicted by Klein[6] and have been previously observed in ZnMn alloys by Martin[17] and by other investigators in CuMn,[1,20] AuMn,[20] and AgMn.[20]

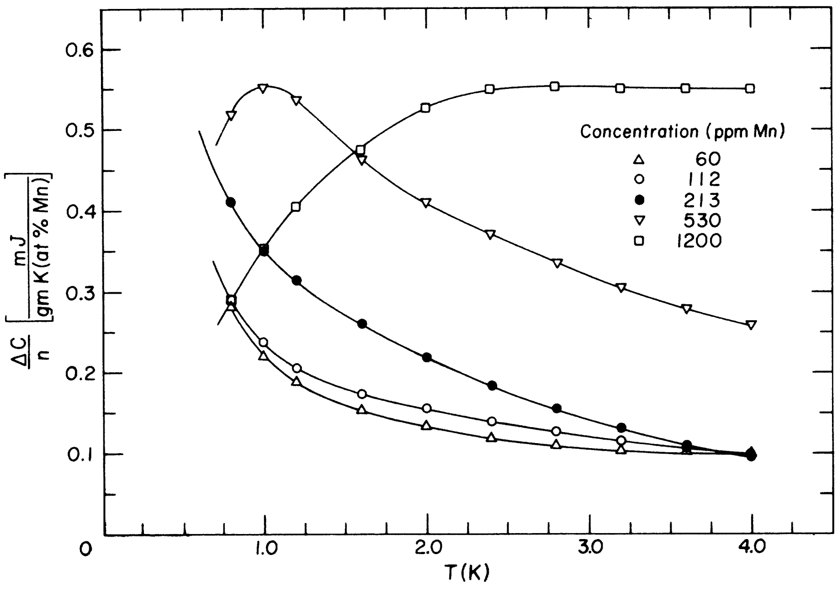

FIG. 2. Excess specific heat per unit concentration, $\Delta C/n$, for five ZnMn alloys plotted as a function of temperature $T$.

Figure 4 is a plot of $\Delta C/n$ as a function of $T/n$ and serves to illustrate the above behavior. Scaling is observed for our three most concentrated alloys, 213, 530, and 1200 ppm Mn, as is apparent from the figure where the data for the three alloys superpose quite accurately in the regions of overlap. The most significant result of these measurements is the proportionality of $\Delta C$ to $n^2/T$ for values of $T/n > 6\times10^{-3}$ (K/ppm). Given the $n^2$ dependence of $\Delta C$, the $T^{-1}$ falloff is just that which the scaling law requires. This is in contrast to the $T^{-2}$ falloff suggested by Marshall.[5] It should be noted that our data for the 60- and 112-ppm-Mn alloys do not obey the scaling law for the specific heat, but show an extra contribution of $\Delta C$ due to single-impurity effects.

We propose a simple empirical expression for $\Delta C$ (as a function of $n$ and $T$) which represents the data accurately in both the low- and high-temperature limits, viz.,

$$\Delta C(n,\ T)=AT/(1+BT^2/n^2)\ , \qquad (2)$$

where $A$ and $B$ are constants independent of $n$ or $T$.

The specific heat described by Eq. (2) obeys the appropriate scaling law of Blandin and Souletie[9,10] for magnetic impurities interacting via a $1/r^3$ potential, namely, $\Delta C/n=f(T/n)$; the excess specific heat per impurity $\Delta C/n$ is a function only of the "reduced temperature" $T/n$.

The proposed expression for $\Delta C(n,\ T)$, Eq. (2), contains the three observations made above, given that $A$ and $B$ are independent of $n$ and $T$:

(a) $\Delta C(T\to 0)=AT$; (b) $T_{\max}=n/(B)^{1/2}$ ;

(c) $\Delta C\,[(B)^{1/2}\,T/n\gg 1]=An^2/BT$ .

From $\Delta C$ we have derived analytic expressions for the entropy $S$, internal energy $U$, free energy $F$, and total entropy change $\Delta S$ using standard thermodynamic relations;

$$S=\int_0^T\left(\frac{\Delta C}{T}\right)dT=\left(\frac{An}{(B)^{1/2}}\right)\tan^{-1}\left(\frac{(B)^{1/2}T}{n}\right)\ , \qquad (3)$$

$$U=\int_0^T\Delta C\,dT=\left(\frac{An^2}{2B}\right)\ln\left[1+B\left(\frac{T}{n}\right)^2\right]\ , \qquad (4)$$

$$F=U-TS=\left(\frac{An^2}{2B}\right)\ln\left[1+B\left(\frac{T}{n}\right)^2\right]-\left(\frac{AnT}{(B)^{1/2}}\right)\tan^{-1}\left(\frac{(B)^{1/2}T}{n}\right)\ , \qquad (5)$$

$$\Delta S=\int_0^\infty\left(\frac{\Delta C}{T}\right)dT=\frac{\pi An}{2(B)^{1/2}}\ . \qquad (6)$$

In the limit $(B)^{1/2}\,T/n\ll 1$, all dependence on concentration disappears and we have $\Delta C=S=AT$, $F=-U=-\frac{1}{2}AT^2$. In the more interesting limit $(B)^{1/2}\,T/n\gg 1$, we obtain for the free energy

$$F=\frac{-\pi AnT}{2(B)^{1/2}}+\left(\frac{An^2}{B}\right)\left[1+\ln\left(\frac{(B)^{1/2}T}{n}\right)\right]\ . \qquad (7)$$

Using a virial expansion valid at high temperature, Larkin and Khmel'nitskii have calculated the linear and quadratic terms in the free energy expressed as a power series in the density of impurities $n$.[7] Using as the interaction between the impurities $V(R)=(V_0/R^3)\cos 2p_0R$ for $p_0R\gg 1$, they obtain for the free energy per unit volume

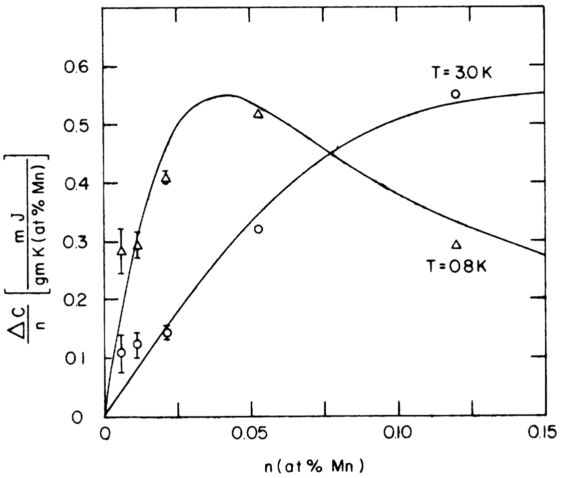

FIG. 3. Excess specific heat per unit concentration, $\Delta C/n$, for five ZnMn alloys as a function of concentration $n$ for two different temperatures. The fit of Eq. (2) to the experimental results is shown as the solid line.

$$F=-nk_BT\ln(2S+1)+\left(\frac{2n^2V_0}{3}\right)\times\left[S(2S+1)\ln\left(\frac{k_BT(a^3n)}{nV_0}\right)-\Phi_2\right]\ ,\tag{8}$$

where $S$ is the spin of the impurity, $\Phi_2$ is a constant, and the cutoff parameter $a$ (on the order of interatomic distances) is such that $a^3n$ is independent of $n$. The first term is the single-impurity contribution to the free energy and is independent of the interaction $V(R)$. The specific heat resulting from the above free energy is

$$C=-T\frac{\partial^2F}{\partial T^2}=\frac{2n^2V_0S(2S+1)}{3T}\ ,\tag{9}$$

which has the same dependence on concentration and temperature as the high-temperature limit of our proposed expression for $\Delta C$ [Eq. (2)] and hence is in agreement with our experimental results.

Equating the terms linear in concentration in Eqs. (7) and (8) we make the following identification: $\pi A/2(B)^{1/2}=k_B\ln(2S+1)$. Using this result in Eq. (6) we obtain the important result that $\Delta S=nk_B\ln(2S+1)$, as expected for the total entropy change of a system of $n$ impurities per unit volume each of spin $S$. Using Eqs. (7) and (8), the coefficients $A$ and $B$ appearing in Eq. (2) can be written as

$$A=\frac{6k_B^2[\ln(2S+1)]^2}{\pi^2V_0S(2S+1)}$$

and (10)

$$B=\left(\frac{3k_B\ln(2S+1)}{\pi V_0S(2S+1)}\right)^2\ .$$

Figure 4 shows the fit of our experimental results for $\Delta C$ to Eq. (2). From this fit we obtain the following empirical results[21]:

$$(A/k_B^2)=2.5\times10^{35}\ (\text{erg cm}^3)^{-1}$$

and

$$(B/k_B^2)=1.3\times10^{37}\ \text{erg}^{-2}\ .$$

We can now determine $\Delta S=\pi An/2(B)^{1/2}$ to be $k_B\ln3.94$ per impurity, which corresponds very closely to a spin $S=\frac{3}{2}$.[22] This agrees with the spin found by Martin from specific-heat measurements[17] on ZnMn, but is less than the value determined

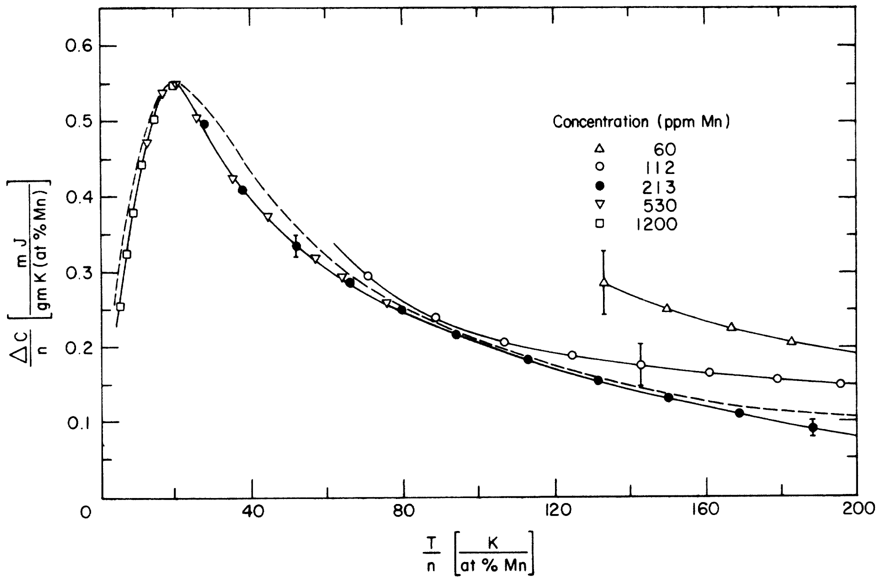

FIG. 4. Excess specific heat per unit concentration, $\Delta C/n$, for five ZnMn alloys plotted as a function of "reduced temperature" $T/n$. The fit of Eq. (2) to the experimental results for the three most comcentrated alloys is shown as the dashed line.

from susceptibility ($S \sim 2$).[14] Using $S = \frac{3}{2}$, Eq. (10) provides two ways to determine $V_0$, the strength of the RKKY interaction. The results are equal to within 2% and yield $V_0 = (0.91 \pm 0.01) \times 10^{-36}$ erg cm$^3$. This $V_0$ for ZnMn from specific-heat measurements is of the same order of magnitude as values of $V_0$ for CuMn ($5 \times 10^{-36}$ erg cm$^3$) and AuMn ($0.22 \times 10^{-36}$ erg cm$^3$) obtained by Larkin *et al.*[23] from the analysis of susceptibility data. Preliminary results from magnetic-susceptibility measurements on these same alloys, when compared with the theory of Larkin and Khmel'nitskii,[7] yield a value of $V_0 = (2.25 \pm 0.20) \times 10^{-36}$ erg cm$^3$ for ZnMn.[24]

It is difficult to draw any firm conclusions from our $\Delta C/n$ data for the 60- and 112-ppm-Mn alloys shown in Figs. 2–4, beyond the simple statement that single-impurity effects are present in these alloys. However, it is also clear, especially from Fig. 2, that concentration-dependent effects due to interactions between Mn impurities are also present for 60 and 112 ppm Mn in the range of temperatures for which $\Delta C$ was measured here. When compared with single-impurity theory for spin $S = \frac{3}{2}$,[25] it is clear that even in the 60-ppm-Mn alloy $\Delta C(T)$ is increasing too rapidly as $T$ decreases. As of yet, no theoretical attempt has been made to calculate the contribution to the specific heat of magnetic impurities in the range of concentration where both single-impurity and impurity-impurity interaction effects are present.

## V. CONCLUSIONS

From measurements of the excess specific heat $\Delta C$ in a series of ZnMn alloys, we have concluded that the results for the three most concentrated alloys, 213, 530, and 1200 ppm Mn, can be satisfactorily understood as due to RKKY interactions between the Mn impurities. We have shown for the first time experimentally that these interactions lead to $\Delta C$ proportional to $n^2/T$ for high $T$ or low $n$. Scaling behavior is observed for $\Delta C/n$ in these three alloys, as predicted by Blandin and Souletie for the RKKY interaction, namely, $\Delta C/n = f(T/n)$. We have proposed a simple analytic expression for the excess specific heat, $\Delta C = AT/(1 + BT^2/n^2)$, and from it have derived expressions for the free energy, internal energy, and entropy. In addition to being in good agreement with our experimental specific-heat results, these thermodynamic functions obey the scaling laws of Blandin and Souletie and coincide with the predictions of Larkin and Khmel'nitskii for the thermodynamic functions at high temperatures of an alloy with interacting magnetic impurities.

Comparing theory and experiment for $\Delta C$, we find $S = \frac{3}{2}$ for the spin of the Mn impurity and $V_0 = (0.91 \pm 0.01) \times 10^{-36}$ erg cm$^3$ for the strength of the RKKY interaction between two Mn impurities. We are continuing our investigation of interactions in these ZnMn alloys by means of magnetic-susceptibility measurements. Preliminary results have yielded $V_0 = (2.25 \pm 0.20) \times 10^{-36}$ erg cm$^3$, as determined from the concentration dependence of the Curie-Weiss temperature.

We hope that the success of our expressions for the thermodynamic functions [Eqs. (2)–(6)] for the spin-glass alloy system ZnMn will encourage other experimentalists to check their applicability to similar alloy systems, such as alloys of Mn in Cu, Ag, and Au. In addition, these thermodynamic functions may provide a stimulus for theoreticians to attack the problem of the low-temperature behavior of the spin glass, in particular, the nature of the collective spin excitations which give rise to the behavior of $\Delta C$ as $T$ tends to zero.

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[22] If our expression for $\Delta C$, Eq. (2), is correct, then it is possible to determine the total entropy change $\Delta S$ for a given alloy from the value of $\Delta C$ at $T_{max}$ alone. The necessary relationship is $\Delta S = \pi \Delta C(T_{max})$. This should be quite useful when specific-heat measurements can only be made over a limited range of temperatures (including $T_{max}$).

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