Specific heat of CuMn at the spin-glass freezing temperature

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The rate of spin-glass entropy increase on heating begins to diminish in the region of the spin-glass freezing temperature (T_f). This is seen most clearly in a plot of (spin-glass specific heat divided by temperature) versus temperature. The spin-glass entropy gained on heating from absolute zero to T_f is roughly equal to that found above T_f. This general behavior has been found for compositions in the range 0.083 to 0.88 at.% Mn.

I. INTRODUCTION

The occurrence of a cusp in the low-field magnetic susceptibility[1] of certain dilute magnetic systems together with the onset of hyperfine splitting in the Mössbauer spectrum[2] and other effects[3] at the same temperature for the same composition has led to the identification of these effects with the so-called spin-glass freezing temperature T_f. If there is some kind of phase change at T_f, then a clear indication would be expected in the spin-glass contribution to specific heat, but this displays a broad anomaly[4] with the maximum at a higher temperature than T_f.

In some recent specific-heat measurements[5] on CuMn below 3 K it was noted, for a 0.083 at.% Mn alloy, that a "knee" in a plot of spin-glass specific heat (C_m) divided by temperature (T) versus T corresponded to the estimated spin-glass freezing temperature.[6,7] The present paper reports measurements to higher temperatures on two more concentrated alloys in which a similar correlation has been observed.

II. EXPERIMENTAL

The preparation of the induction-melted, chill-cast, and homogenized alloys is described elsewhere,[5] where the analysis results are also given. The present measurements were made in an apparatus described elsewhere,[8] and the graphs of results also include data points from the earlier work below 3 K.[5] Two sets of measurements in the 2.5-to-30 K range, with intermediate warming to room temperature, were made on a Cu−0.88 at.% Mn alloy while a single run was made on a Cu−0.43 at.% Mn alloy. However, in the latter case the region around T_f was measured twice.

III. RESULTS

The new results are represented by the least-squares-fitted polynomials given in Table I, the deviation of the raw data from these polynomials being shown in Fig. 1. (The fit for the 0.88 at.% Mn alloy is considered good; the deviations seen in Fig. 1 are

TABLE I. Polynomial coefficients representing specific heat $C_p = \sum a_n T^n$. Units cal/K g atom (1 cal = 4.186 J). Each polynomial reproduces the smoothed specific heat to within 0.01%.

Pure Cu	Cu−0.43 at.% Mn	Cu−0.88 at.% Mn
$a_1 = +0.165\,794 \times 10^{-3}$	$a_{-2} = +0.689\,145\,118 \times 10^{-5}$	$a_{-2} = +0.142\,023\,08 \times 10^{-4}$
$a_3 = +0.113\,549 \times 10^{-4}$	$a_1 = +0.469\,708\,485 \times 10^{-3}$	$a_1 = +0.510\,740\,02 \times 10^{-3}$
$a_5 = +0.269\,085 \times 10^{-9}$	$a_2 = +0.669\,774\,732 \times 10^{-3}$	$a_2 = +0.464\,401\,54 \times 10^{-3}$
$a_7 = +0.253\,298 \times 10^{-10}$	$a_3 = -0.247\,508\,525 \times 10^{-3}$	$a_3 = -0.658\,094\,28 \times 10^{-4}$
$a_9 = -0.435\,063 \times 10^{-13}$	$a_4 = +0.540\,885\,923 \times 10^{-4}$	$a_4 = +0.634\,165\,75 \times 10^{-6}$
$a_{11} = +0.263\,103 \times 10^{-16}$	$a_5 = -0.405\,572\,598 \times 10^{-5}$	$a_5 = +0.167\,222\,10 \times 10^{-5}$
$a_{13} = -0.495\,026 \times 10^{-20}$	$a_6 = -0.671\,904\,424 \times 10^{-6}$	$a_6 = -0.225\,576\,54 \times 10^{-6}$
	$a_7 = +0.195\,377\,142 \times 10^{-6}$	$a_7 = +0.739\,268\,36 \times 10^{-8}$
	$a_8 = -0.218\,660\,232 \times 10^{-7}$	$a_8 = +0.713\,224\,11 \times 10^{-9}$
	$a_9 = +0.140\,414\,025 \times 10^{-8}$	$a_9 = -0.787\,874\,07 \times 10^{-10}$
	$a_{10} = -0.556\,442\,182 \times 10^{-10}$	$a_{10} = +0.320\,157\,19 \times 10^{-11}$
	$a_{11} = +0.134\,756\,467 \times 10^{-11}$	$a_{11} = -0.618\,449\,31 \times 10^{-13}$
	$a_{12} = -0.183\,295\,565 \times 10^{-13}$	$a_{12} = +0.472\,809\,26 \times 10^{-15}$
	$a_{13} = +0.107\,472\,921 \times 10^{-15}$	
Symbol in figures	× ▷	+ □ ◇

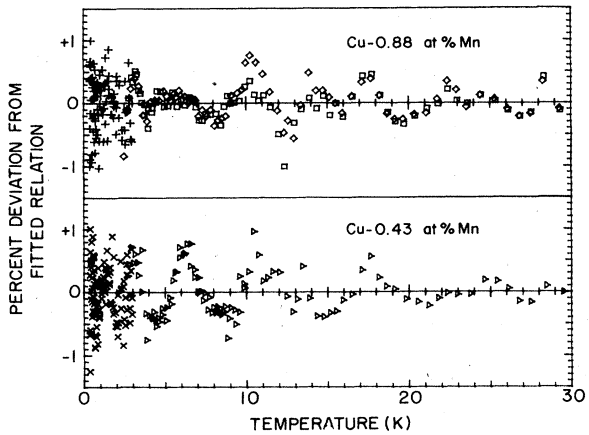

FIG. 1. Deviation of the raw specific-heat data from the polynomial fits given in Table I.

associated with defects in the temperature scale; see for example Ref. 9. The fit for the 0.43 at.% Mn alloy is also good except in the region of T_f.) To obtain the spin-glass specific heat, the specific heat of pure copper and the nuclear specific heat were subtracted. The coefficients for the pure copper are given in Table I and were obtained from a least-squares fit to the data in Refs. 8 and 10. The nuclear specific heat is as detailed in Ref. 5. For these more concentrated alloys, with the wide temperature range up to 30 K, the specific heat of pure copper only approximates the non-spin-glass specific heat. However, it is probably a reasonable approximation since, up at least to the spin-glass freezing temperature, the spin-glass specific heat is greater than the specific heat of copper. (It has been shown that the addition of Mn to Cu results in significant changes to the elastic constants,[11] while the shape of the lattice-vibration spectrum will also change. The elastic-constant change corresponds to an increase of lattice specific heat at low temperatures of about 0.45% for the 0.88 at.% Mn alloy. The electronic specific heat will probably also increase slightly.[5])

IV. DISCUSSION

The results plotted as spin-glass specific heat versus temperature (Fig. 2) do not show any feature at T_f. [Irregularities at higher temperatures correspond to defects in the temperature scale (amplified because the smoothed specific heat of copper has been subtracted) and are not significant.] However, the plot of C_m/T vs T (Fig. 3) shows that T_f corresponds to the onset of an initially linear decline in C_m/T at higher temperatures. The area under the plot of Fig. 3 corresponds to the entropy, and thus the results show that above T_f the rate of increase of entropy begins to decrease rapidly. Uncertainty regarding the non-spin-glass specific heat at the highest

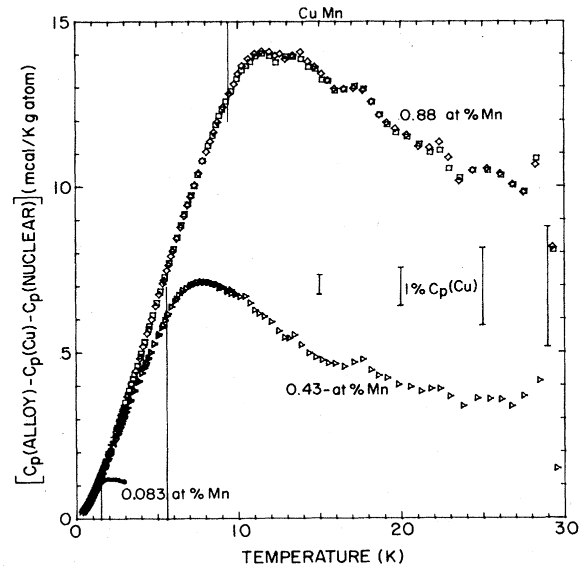

FIG. 2. Spin-glass specific heat plotted against temperature. The vertical bars intersecting the plots mark the estimate of T_f for each composition. The bars in the center of the graph show the magnitude of 1% of the specific heat of copper.

temperatures (see discussion above) makes an accurate total entropy estimate impossible. However, it appears that only about half the total spin-glass entropy is taken up in heating from absolute zero to T_f. (The total entropy per gram atom of Mn corresponds roughly to R ln 4 or spin $J=\frac{3}{2}$. If the anomaly does have a long, high-temperature tail, then an entropy of R ln5 or spin $J=2$ is possible.)

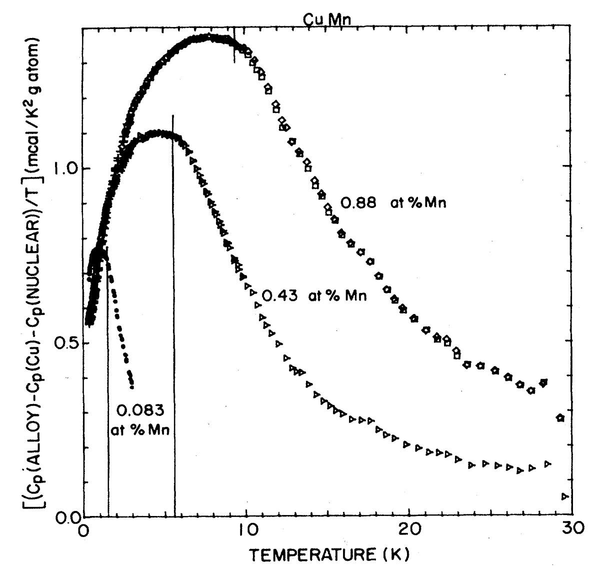

FIG. 3. (Spin-glass specific heat divided by temperature) plotted against temperature. The vertical bars intersecting the plots mark the estimate of T_f for each composition.

The present work is believed to be the first time that a clear feature in the specific heat of CuMn has been seen at T_f. The earlier work of Wenger and Keesom[4] was on 1.2 and 2.4 at.% Mn alloys and a C_p/T vs T^2 plot (where C_p is the total specific heat) showed no feature at T_f. The present work suggests that the "knee" becomes less sharp as the Mn content increases, and the plot against T^2 would also tend to smear the effect. Another possible difference is that the present alloys were chill cast and very homogeneous,[5] whereas the samples of Ref. 4 were "grown in an rf crystal grower," suggesting slow solidification from the melt and consequently larger concentration gradients. However, it appears that susceptibility cusps were observed in measurements on the actual specific-heat samples.[4] Mydosh[12] has briefly reported a reanalysis of early specific-heat data and has concluded that "at best" there is "some" correlation between a knee or maximum in C_m/T and T_f. By contrast the present work has shown a very clear effect for CuMn. The cusp in the low-field ac susceptibility is very sharp, but it has been suggested[3] that it is caused by the sudden freezing of a few large magnetic clusters which would have little effect on the specific heat, which represents an integral over the whole sample. However, the specific-heat feature observed in the present work is fairly narrow and is centered at temperature T_f, suggesting that something rather fundamental is occurring in the region of T_f.

There is still controversy regarding the significance of the spin-glass freezing temperature T_f. Is there a genuine phase change here or is there just a gradual freezing in of spins as the temperature is lowered? It has been pointed out[6] that the low-field ac-susceptibility cusp is not an equilibrium observation while any phase transition would be between equilibrium states. In some alloy systems and composition ranges, different properties may have different freezing temperatures.[6,13] For some systems the temperature of the cusp in the low-field ac susceptibility may be frequency dependent,[14] whereas for other systems the position is independent of frequency.[15,16] (Measurements at dc have also been made.[17]) A magnetic field will broaden and shift the position of the cusp, and it has been suggested that this may account for the apparent frequency dependence of electron-spin-resonance results.[15] Neutron scattering results[18] were interpreted as showing that the freezing temperature for a magnetic cluster depended on its size. However, these results have been reinterpreted[19] as showing a sharp transition at T_f. It has been suggested that a frequency-dependent T_f is associated with systems showing clustering (either chemical or physical) involving interactions between the transition-metal atoms.[20] A frequency-dependent T_f could be consistent with a phase transition for which the true T_f is obtained from an experiment with an infinitely long time scale.[21]

The explanation of the various features observed at T_f is a major preoccupation of theoreticians.[22] Attempts to explain the lack of a cusp in the specific heat have been made with a magnetic-cluster model.[23] However, this approach has been criticized[4,6] on the grounds that the number of clusters and free spins assumed to be present at different temperatures are not consistent with other observations. An alternative approach has been proposed[6] where there is short-range antiferromagnetic coupling above T_f gradually decreasing with increasing temperature. Clearly the feature reported in the present work will be a further restriction on possible theories. Another problem raised by the theoreticians is whether the postulated spin-glass phase transition could occur in a system with only three dimensions.[21] However, recent numerical-simulation work[24] shows no qualitative difference in results from two to five dimensions. These authors[24] also suggest that there is a slow relaxation into the ordered state and that there is probably a phase transition at a nonzero T_f. Perhaps the situation could be compared to the development of order below the critical temperature for an order-disorder transition which is a sluggish phase change in the direction of order and where short-range order exists above the transition temperature.

V. CONCLUSION

The observation of a specific-heat feature in the region of T_f for CuMn (present work) and also for AuFe (Ref. 25) would appear to lend support to the idea of a high-order phase transition at T_f. This could, perhaps, be of the subtle type portrayed by NMR studies of spin-glass dynamics[26] where there is a gradual freezing of spins on cooling, but the motions are highly correlated below T_f.

Note added in proof. Recent neutron scattering results[27] on Cu−4.7 at.% Mn yield spin $J = 1.77 \pm 0.05$. This value is shown to agree quite well with values (1.73−2.14) obtained elsewhere by high-temperature susceptibility measurements for a large range of CuMn compositions (0.02 to 11 at.% Mn). The present specific-heat result is in accord with these values.

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