PHYSICAL REVIEW B VOLUME 32, NUMBER 1 1 JULY 1985

Specific heat of dilute Cu-Mn alloys in the region of the spin-glass freezing temperature

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(Received 16 January 1985)

Specific-heat measurements in the 0.35—3-K temperature range on several Cu-Mn alloys are reported. The alloys, lying in the composition range 0.045—0.085 at. % Mn, were made in two different ways. It was found that the specific heat in the region of the spin-glass freezing temperature was strongly dependent on the degree of homogenization of the sample. In all cases a "knee" was observed in a plot of (magnetic specific heat)/(temperature) versus temperature. For well-homogenized samples the position of the "knee," as a function of composition, is consistent with the known spin-glass freezing temperature as determined by other methods. The results show how sensitive these alloys are to oxidation and Mn evaporation during both preparation and heat treatment.

INTRODUCTION

In dilute metallic magnetic systems, such as Cu-Mn (where the moment is carried on the Mn atom), the moments interact via the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. The random distribution of Mn atoms in the matrix means that at the lowest temperatures the moments are frozen in apparently random directions determined by their interaction with the other moments in the alloy, hence, the term "spin glass."[1] Clearly, the rotation of one moment will have an effect on all other moments and a long equilibrium time may be expected with the possibility of a nonunique equilibrium state. (A possible complication is the Kondo,[2] or single-impurity, effect where, at a sufficiently low temperature, the electron spins interact with the impurity spins in such a way that the effective impurity spin is zero. This will not be a factor in the present work since the "Kondo temperature" for Cu-Mn is about 0.001 K, far below the range of the measurements to be reported here.)

The spin-glass systems have been known for many years to show curious magnetic properties as well as anomalies in the electrical resistance and specific heat. Renewed interest was sparked by the discovery of a sharp cusp in the low-field ac susceptibility[3] and discussion since has centered on whether this marks the boundary of a "spin-glass phase" or whether it is an artifact connected with a rapidly increasing equilibrium time as the temperature is decreased.[4] If the former, then some effect should be seen in the specific heat for which the "magnetic contribution" (C_M) displays a broad anomaly with maximum well above the "susceptibility cusp temperature" or "freezing temperature" (T_f).[5] Some years ago it was reported[6] that there was a "knee" at T_f in a plot of (C_M/T) versus T for a Cu-0.083 at. % Mn alloy. Further work showed more rounded effects for two more concentrated Cu-Mn alloys (0.43 and 0.88 at. % Mn) (Ref. 5) and a well-defined "knee" for an Au-1 at. % Fe alloy,[7] all at the appropriate T_f value for their composition. More recently Fogle *et al.*[8] published results on a Cu-0.279 at. % Mn alloy where they found a more subtle feature in the region of T_f. While it is important that both laboratories agree that there is an effect on the magnetic specific heat at T_f, possibly corresponding to a higher-order phase transition, it seemed worthwhile to extend the measurements to see whether this effect is just a function of the Mn content of the alloy or whether it depends on the perfection of the sample. (Thus, more concentrated alloys might be inherently less perfect owing to clustering or short-range-order effects.[9])

The initial objective of the present work was to make alloys with the same composition by two different methods. However, for reasons detailed below, a different approach was eventually used. In this approach a previously measured chill-cast and homogenized sample was remelted to produce a "slow-cooled" sample. (The concentration gradients in such a sample might be lower than those possible if the sample were prepared directly from the component metals.) The alloy was then measured "as cast" and after homogenization. Quite large changes in C_M in the region around T_f were observed but it was possible to return the specific heat to the original values with sufficient homogenization. Thus, the specific heat in the region of T_f does depend on the thermal history of the sample. Furthermore, the results lend support to the previous hypothesis that the "knee" in the plot of (C_M/T) versus T does correspond to T_f.

EXPERIMENTAL

The specific-heat measurements were made in the apparatus used for our previous Cu-Mn work[6] and described elsewhere. All measurements were made in the ambient magnetic field ($\sim$0.03 mT outside the cryostat). In most cases two separate runs were made on each sample with an intermediate warm to room temperature. Each such run was allocated a separate symbol in the figures. The laboratory had been relocated since the previous work[6] and the equipment was checked by measurement of a $\sim$140-g vacuum cast pure copper sample used previously. The results of these measurements are shown in Fig. 1 and Table III and have been used as the copper contribution in determining the magnetic contributions to specific heat of the Cu-Mn alloys. The original intention was to make al-

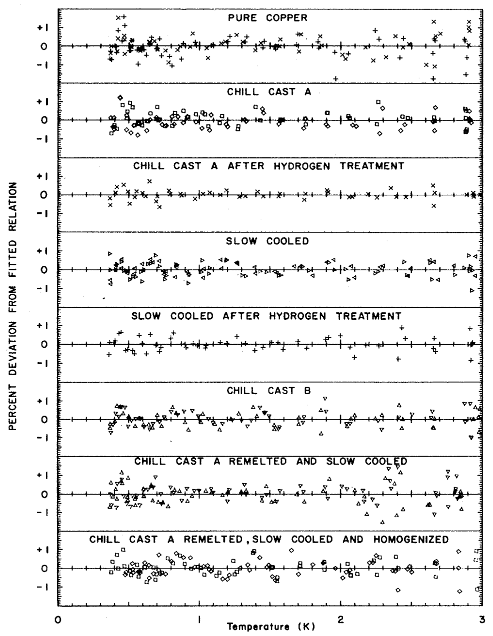

FIG. 1. Percentage deviations of the raw specific-heat data for copper and the nominal 0.075 at.% Mn samples from the polynomial fits given in Table III.

loys, of nominal composition 0.075 at.% Mn and of identical final composition, by (i) chill casting and (ii) slow cooling the sample from the melt. The chill-cast sample (sample A) was induction melted in a hydrogen atmosphere, to reduce any oxide, as described in Ref. 6 and using the same starting materials. (The hydrogen was pumped off before casting. If this is not done the sample produced is a metal "sponge" because the hydrogen comes out of solution as the sample solidifies.) The "slow-cooled" sample was prepared in the same way except that it was allowed to cool relatively slowly (in the alumina crucible in which it had been melted) after the induction furnace was shut off. The alloys were then homogenized (sealed in a hydrogen atmosphere, ~30 days at ~1000°C) and degassed as described in Ref. 6. (Note, any hydrogen in the sample is liable to affect the specific heat.[10]) Pieces were cut from each end of each sample for chemical analysis. The Mn content was determined by a new method, inductively coupled plasma—atomic emission spectroscopy, and showed very similar Mn contents for the two samples (analysis 1, Table I). (There is normally a Mn loss owing to evaporation.[6]) However, the specific-heat results, to be detailed later, indicated much more Mn in the slow-cooled sample. It was therefore suspected that some oxidation of Mn had occurred and both samples were hydrogen treated at high temperatures in an attempt to reduce the suspected oxide. This was done by cleaning the samples[6] and placing them on a broken alumina crucible in a quartz tube containing a flowing atmosphere of purified hydrogen. The treatment on several successive days was for a total of about 30 hours at 1000°C. The samples were then outgassed as before.[6] The specific heat of each sample was remeasured and found to be slightly lower than before in each case, which would be consistent with a slight loss of Mn (by evaporation) during the hydrogen treatment. At this stage the chemical analysis was still not suspect and a second chill-cast sample (B) was prepared exactly as before. This gave results slightly lower than the chill-cast sample (A). Pieces for analysis were cut from this sample and the hydrogen-treated slow-cooled sample. This analysis (Table I, analysis 2) showed much more Mn in the slow-cooled sample than in the chill-cast sample, and was consistent with the specific-heat data to be presented later. Furthermore the Mn content for the slow-cooled sample was about 30% more than the previous analysis for the same sample taken before hydrogen treatment (which the specific-heat data suggest resulted in a loss of Mn, presumably by evapora-

TABLE I. Analysis results for Mn content in atomic % for nominal 0.075 at.% Mn samples. [*Note*: Each result is based on several determinations and the error limits (where stated) refer to the scatter of the individual determinations. For these dilute alloys the analysts expect the absolute error to be several times greater than the error limits stated here.]

Sample	Analysis number 1	2	3	4	5	Best value[a]	Approximate weight of specific-heat sample g
Chill cast A	0.0493 ± 0.0006 0.0512 ± 0.0009		0.061_3 0.062_4	0.060_1 0.060_1	$0.055_5\pm0.001$ $0.056_7\pm0.001$	0.059	78
Chill cast A after H_2 treatment					$0.052_0\pm0.001$ $0.052_0\pm0.001$	0.052	78
Slow cool	0.0502 ± 0.0004 0.0566 ± 0.0007		0.065_9 0.064_8	0.063_6 0.063_6	$0.061_3\pm0.001$ $0.062_4\pm0.001$	0.064	115
Slow cool after H_2 treatment		0.068_2 0.072_9	0.065_9 0.070_5			0.069	111
Chill cast B		0.047_4 0.045_1	0.046_2 0.045_1			0.046	105

[a] Results of analysis 1 are ignored.

tion). There was now considerable doubt as to the validity of the chemical analysis of Mn and the samples used for analysis 1 were reanalyzed (analysis 3, Table I). This showed large differences from the previous analysis results and a further analysis (analysis 4, Table I) was run on these same samples the next day. Finally, these same samples were run with a new sample some time later (analysis 5, Table I).

If we ignore the results of analysis 1 (which, for reasons unknown, was approximately 20% lower on the basis of later results) it will be seen that there is a steady drift to lower values on repeated analysis of the same sample. This drift is several times the error limit given in the final analysis (analysis 5, Table I) and corresponds to a change of around 10%. This is of the order of absolute accuracy the analysts expect for the method for these dilute alloys (see note on Table I). Furthermore, there is still a problem in that the analysis results indicate similar Mn contents for the chill-cast A and slow-cooled samples, whereas the specific-heat data suggest much larger differences. The discrepancies between the various analysis results and between analysis and specific-heat data could be attributed to inhomogeneous samples, loss of Mn by oxidation or during sample cleaning, or to errors in the analytical or specific-heat measurements. The first reason seems unlikely because random results would be expected rather than the steady drifts observed. The last is also ruled out because two independent sets of measurements are normally made on each sample with very reproducible results ($\sim\pm0.1\%$). Hence, the sample handling procedures or analytical results are suspect. From an examination of Table I it would seem unwise to assign more than one significant figure accuracy to the results given there.

An impurity analysis was also run on each sample and is given in Table II. It is unlikely that the impurity levels found would have any significant effect on the specific-heat results.

It may be concluded that the loss of Mn during alloy preparation is quite different for the two methods used (chill cast and slow cool), presumably because of the large surface of molten alloy exposed to the vacuum during casting in the former method and consequent loss of the high vapor pressure Mn by evaporation. Hence, it was not possible to compare alloys of identical composition made by the two methods. Another approach was therefore used. The chill-cast alloy (sample A) was remelted and allowed to cool slowly in the melting crucible to produce a new slow-cooled sample. After measuring the specific heat, this sample was homogenized (approximately 66 days at 1000 °C), degassed, and remeasured when the specific heat was found to be essentially the same as for the original chill-cast starting material.

In an attempt to investigate the homogenization procedure more fully, a chill-cast and homogenized 0.083 at. % Mn alloy, measured previously,[6] was remeasured and then remelted and allowed to cool slowly. After measurement it was homogenized for periods of 1, 7, and 30 days at 1000 °C, being degassed and remeasured after each homogenization period. There were two mishaps during this sequence of heat treatment. Firstly, owing to a misunderstanding, the first (one-day) homogenization was done in an atmosphere of flowing hydrogen rather than in a sealed quartz tube containing hydrogen. This resulted in considerable Mn loss as judged from the specific-heat results (see later). Secondly, a quartz tube cracked during the final degassing and the vacuum was observed to be in the region of 10^{-4} mm Hg at the highest temperature instead of the normal 10^{-6}. It was found that the specific heat was low, suggesting oxidation of Mn. To check this, the sample was held at 1000 °C in flowing purified hydrogen for a total of 23 hours, then degassed and remeasured. The results obtained substantially confirmed those obtained previously on the more dilute alloy but also showed how sensitive these alloys are to evaporation and oxidation.

It should be emphasized that the various starting materials and samples were carefully cleaned before any heat treatment[6] and a dummy run up to temperature (to degas) was made with the melting apparatus before loading the material to be melted.

RESULTS

Specific-heat measurements were made on the various samples described in the previous section. The molar specific heat was calculated by assuming that all the nominal 0.075 at. % Mn samples were, in fact, ~0.05 at. % Mn when the "average atomic weight" is 63.536. For the 0.083 at. % Mn sample the value 63.53 used previously[6] was taken. The approximate sample weights are given in

TABLE II. Impurity analysis (parts per million by weight) for nominal 0.075 at. % Mn samples.

Sample	Mg	Al	Si	Fe	Ag	Method
Chill cast A	0.1–0.9	<0.3	0.6–6.0	0.3–3.0	<0.01	1[a]
	0.03–0.3	<0.3	0.3–3.0	0.1–1.0	<0.01	
Slow cool	0.03–0.3	<0.3	0.6–6.0	0.1–1.0	<0.01	1[a]
	0.03–0.3	<0.3	1.0–9.0	0.1–1.0	<0.01	
Slow cool after H_2 treatment	0.006–0.06	0.1–0.9	4–40	0.3–2.4	0.03–0.3	2[b]
	0.01–0.12	0.1–0.9	10–90	0.3–3.0	0.06–0.6	
Chill cast B	0.02–0.15	0.6–6.0	0.03–0.3	0.1–1.2	0.3–3.0	2[b]
	0.01–0.12	0.3–2.5		0.3–3.0	0.6–6.0	

[a] Optical emission spectrography.

[b] Mass spectrography.

TABLE III. Pure copper and nominal 0.075 at. % Mn samples. 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%.

Sample	Coefficients	Symbols in figures
Pure copper	$a_1 = +0.165\,23 \times 10^{-3}$ $a_3 = +0.113\,08 \times 10^{-4}$	+ ×
Chill cast A	$a_1 = +0.882\,657\,99 \times 10^{-3}$ $a_3 = +0.176\,145\,67 \times 10^{-3}$ $a_5 = -0.509\,191\,62 \times 10^{-3}$ $a_7 = +0.334\,440\,08 \times 10^{-3}$ $a_9 = -0.114\,704\,12 \times 10^{-3}$ $a_{11} = +0.229\,720\,16 \times 10^{-4}$ $a_{13} = -0.269\,347\,10 \times 10^{-5}$ $a_{15} = +0.171\,179\,68 \times 10^{-6}$ $a_{17} = -0.455\,080\,96 \times 10^{-8}$	□◇
Chill cast A after H_2 treatment	$a_1 = +0.881\,094\,39 \times 10^{-3}$ $a_3 = +0.163\,188\,71 \times 10^{-3}$ $a_5 = -0.517\,962\,74 \times 10^{-3}$ $a_7 = +0.336\,457\,26 \times 10^{-3}$ $a_9 = -0.101\,818\,01 \times 10^{-3}$ $a_{11} = +0.119\,057\,68 \times 10^{-4}$ $a_{13} = +0.142\,952\,99 \times 10^{-5}$ $a_{15} = -0.667\,198\,50 \times 10^{-6}$ $a_{17} = +0.920\,978\,73 \times 10^{-7}$ $a_{19} = -0.593\,860\,35 \times 10^{-8}$ $a_{21} = +0.151\,268\,22 \times 10^{-9}$	×
Slow cooled	$a_1 = +0.100\,886\,684 \times 10^{-3}$ $a_2 = +0.581\,687\,189 \times 10^{-2}$ $a_3 = -0.174\,933\,987 \times 10^{-1}$ $a_4 = +0.288\,739\,961 \times 10^{-1}$ $a_5 = -0.285\,045\,038 \times 10^{-1}$ $a_6 = +0.173\,288\,024 \times 10^{-1}$ $a_7 = -0.653\,667\,537 \times 10^{-2}$ $a_8 = +0.148\,964\,372 \times 10^{-2}$ $a_9 = -0.187\,564\,384 \times 10^{-3}$ $a_{10} = +0.999\,624\,694 \times 10^{-5}$	◁ ▷
Slow cooled after H_2 treatment	$a_1 = +0.167\,101\,64 \times 10^{-4}$ $a_2 = +0.608\,082\,48 \times 10^{-2}$ $a_3 = -0.170\,712\,27 \times 10^{-1}$ $a_4 = +0.259\,488\,94 \times 10^{-1}$ $a_5 = -0.232\,263\,57 \times 10^{-1}$ $a_6 = +0.124\,351\,14 \times 10^{-1}$ $a_7 = -0.391\,224\,60 \times 10^{-2}$ $a_8 = +0.667\,336\,08 \times 10^{-3}$ $a_9 = -0.476\,414\,50 \times 10^{-4}$	+
Chill cast B	$a_1 = +0.878\,607\,15 \times 10^{-3}$ $a_3 = +0.226\,035\,81 \times 10^{-3}$ $a_5 = -0.786\,806\,91 \times 10^{-3}$ $a_7 = +0.646\,252\,68 \times 10^{-3}$ $a_9 = -0.282\,969\,64 \times 10^{-3}$ $a_{11} = +0.745\,499\,44 \times 10^{-4}$ $a_{13} = -0.121\,299\,31 \times 10^{-4}$ $a_{15} = +0.119\,114\,85 \times 10^{-5}$ $a_{17} = -0.646\,437\,77 \times 10^{-7}$ $a_{19} = +0.148\,772\,29 \times 10^{-8}$	△▽

TABLE III. (*Continued*).

Sample	Coefficients	Symbols in figures
Chill cast A, remelted and slow cooled	$a_1=+0.497\,831\,01\times10^{-3}$	△▽
	$a_2=+0.254\,347\,43\times10^{-2}$	
	$a_3=-0.588\,151\,12\times10^{-2}$	
	$a_4=+0.608\,707\,32\times10^{-2}$	
	$a_5=-0.353\,294\,06\times10^{-2}$	
	$a_6=+0.117\,690\,35\times10^{-2}$	
	$a_7=-0.209\,045\,78\times10^{-3}$	
	$a_8=+0.152\,885\,40\times10^{-4}$	
Chill cast A, remelted slow cooled, and homogenized	$a_1=+0.882\,217\,18\times10^{-3}$	□◊
	$a_3=+0.195\,465\,43\times10^{-3}$	
	$a_5=-0.593\,079\,92\times10^{-3}$	
	$a_7=+0.424\,595\,48\times10^{-3}$	
	$a_9=-0.162\,960\,85\times10^{-3}$	
	$a_{11}=+0.378\,886\,88\times10^{-4}$	
	$a_{13}=-0.547\,346\,65\times10^{-5}$	
	$a_{15}=+0.479\,446\,98\times10^{-6}$	
	$a_{17}=-0.232\,825\,89\times10^{-7}$	
	$a_{19}=+0.480\,230\,04\times10^{-9}$	

Table I. The results for each sample (or each condition of each sample) were fitted to various polynomial series and that showing the smallest least-squares deviation was chosen to represent the results. These polynomials are listed in Tables III and IV for the nominal 0.075 at. % Mn and the 0.083 at. % Mn samples, respectively, and deviations of the raw specific heat from these fits are shown in Figs. 1 and 2, respectively. Results for pure copper are also shown at the top of Fig. 1 and these deviations reflect small temperature scale errors which should be present in the other fits. In general this is not exactly so and hence the fitted polynomials only approximate (within a few tenths of a percent) the true specific heat.

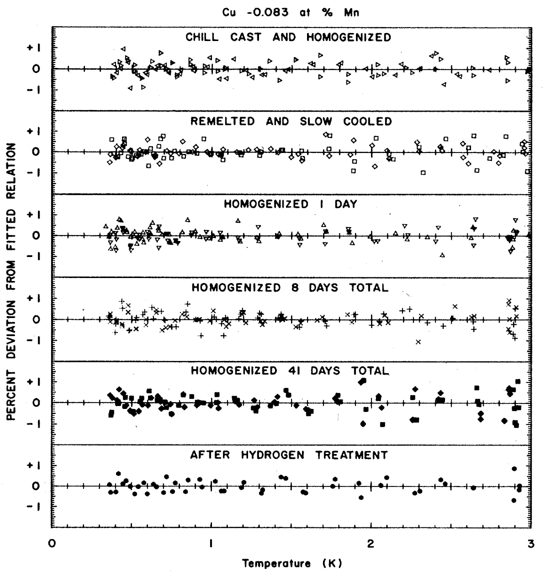

FIG. 2. Percentage deviations of the raw specific-heat data for the 0.083 at. % Mn sample from the polynomial fits given in Table IV.

DISCUSSION

The magnetic contribution to specific heat (C_M) was obtained by subtracting the specific heat of copper (Table III) from the molar specific-heat values together with a very small nuclear specific-heat contribution, determined as discussed in Ref. 6, the coefficient for which was taken as 0.639 μcal K/g-atom for the nominal 0.075 at. % Mn alloys and as 1.06 μcal K/g-atom for the 0.083 at. % Mn alloy. Errors in the magnetic specific heat, resulting from slight errors in the nuclear term, should be less than 0.2% above 0.5 K. Errors in assuming that the electronic and lattice parts of the alloy specific heat are the same as for pure copper should be negligibly small.[6]

The magnetic specific heat for the nominal 0.075 at. % alloys is shown in Fig. 3. The topmost curve (◁ ▷) is the slow-cooled sample after homogenization for which the "best value" for Mn content (Table I) is 0.064 at. % Mn. The next curve (+) is the same alloy after hydrogen treatment for which the chemical analysis result is 0.069 at. % Mn although the specific-heat results indicate a slight loss of Mn, which is quite probable (evaporation owing to high vapor pressure at ~1000 °C, the temperature of the hydrogen treatment). The next two curves are for the chill-cast A sample before (□◊) and after (×) hydrogen treatment. The corresponding chemical analysis results are 0.059 and 0.052 at. % Mn, respectively. The lowest curve (△ ▽) is for the chill-cast B sample (0.046 at. % Mn). It will be observed that the curve positions do not scale well with the chemical analysis results.

Figure 3 also shows that the magnetic specific heat displays the usual broad anomaly with the position of the maximum moving to higher temperature as the Mn con-

TABLE IV. Cu-0.083 at.% Mn sample. 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%.

Sample	Coefficients	Symbols in figures
Chill cast	$a_1 = +0.530\,294\,2 \times 10^{-3}$	◁ ▷
	$a_2 = +0.164\,284\,8 \times 10^{-2}$	
	$a_3 = -0.249\,114\,4 \times 10^{-2}$	
	$a_4 = +0.135\,894\,0 \times 10^{-2}$	
	$a_5 = +0.617\,788\,7 \times 10^{-3}$	
	$a_6 = -0.120\,097\,0 \times 10^{-2}$	
	$a_7 = +0.615\,861\,9 \times 10^{-3}$	
	$a_8 = -0.139\,363\,3 \times 10^{-3}$	
	$a_9 = +0.119\,702\,4 \times 10^{-4}$	
Remelted and slow cooled	$a_1 = +0.467\,444\,14 \times 10^{-3}$	□◇
	$a_2 = +0.255\,196\,87 \times 10^{-2}$	
	$a_3 = -0.650\,112\,72 \times 10^{-2}$	
	$a_4 = +0.965\,435\,93 \times 10^{-2}$	
	$a_5 = -0.884\,099\,95 \times 10^{-2}$	
	$a_6 = +0.493\,443\,05 \times 10^{-2}$	
	$a_7 = -0.163\,218\,75 \times 10^{-2}$	
	$a_8 = +0.294\,022\,28 \times 10^{-3}$	
	$a_9 = -0.222\,179\,24 \times 10^{-4}$	
Homogenized one day	$a_1 = +0.442\,580\,4 \times 10^{-3}$	△▽
	$a_2 = +0.245\,735\,4 \times 10^{-2}$	
	$a_3 = -0.525\,597\,6 \times 10^{-2}$	
	$a_4 = +0.604\,872\,4 \times 10^{-2}$	
	$a_5 = -0.395\,969\,4 \times 10^{-2}$	
	$a_6 = +0.144\,407\,3 \times 10^{-2}$	
	$a_7 = -0.273\,079\,9 \times 10^{-3}$	
	$a_8 = +0.208\,898\,9 \times 10^{-4}$	
Homogenized eight days total	$a_1 = +0.364\,769\,5 \times 10^{-3}$	+ ×
	$a_2 = +0.298\,316\,8 \times 10^{-2}$	
	$a_3 = -0.662\,410\,5 \times 10^{-2}$	
	$a_4 = +0.793\,610\,4 \times 10^{-2}$	
	$a_5 = -0.540\,955\,9 \times 10^{-2}$	
	$a_6 = +0.206\,186\,0 \times 10^{-2}$	
	$a_7 = -0.409\,543\,3 \times 10^{-3}$	
	$a_8 = +0.330\,819\,2 \times 10^{-4}$	
Homogenized 41 days total	$a_1 = +0.707\,207\,21 \times 10^{-3}$	■◆
	$a_2 = -0.355\,771\,52 \times 10^{-3}$	
	$a_3 = +0.347\,671\,42 \times 10^{-2}$	
	$a_4 = -0.860\,283\,42 \times 10^{-2}$	
	$a_5 = +0.990\,272\,03 \times 10^{-2}$	
	$a_6 = -0.527\,207\,19 \times 10^{-2}$	
	$a_7 = +0.312\,275\,45 \times 10^{-3}$	
	$a_8 = +0.109\,431\,94 \times 10^{-2}$	
	$a_9 = -0.570\,436\,78 \times 10^{-3}$	
	$a_{10} = +0.120\,518\,55 \times 10^{-3}$	
	$a_{11} = -0.964\,593\,00 \times 10^{-5}$	
After H_2 treatment	$a_1 = +0.872\,158\,483 \times 10^{-3}$	●
	$a_2 = -0.101\,242\,896 \times 10^{-2}$	
	$a_3 = +0.609\,720\,957 \times 10^{-2}$	
	$a_4 = -0.157\,265\,254 \times 10^{-1}$	
	$a_5 = +0.217\,556\,114 \times 10^{-1}$	
	$a_6 = -0.177\,252\,005 \times 10^{-1}$	
	$a_7 = +0.874\,155\,469 \times 10^{-2}$	
	$a_8 = -0.256\,545\,478 \times 10^{-2}$	
	$a_9 = +0.412\,563\,889 \times 10^{-3}$	
	$a_{10} = -0.280\,097\,541 \times 10^{-4}$	

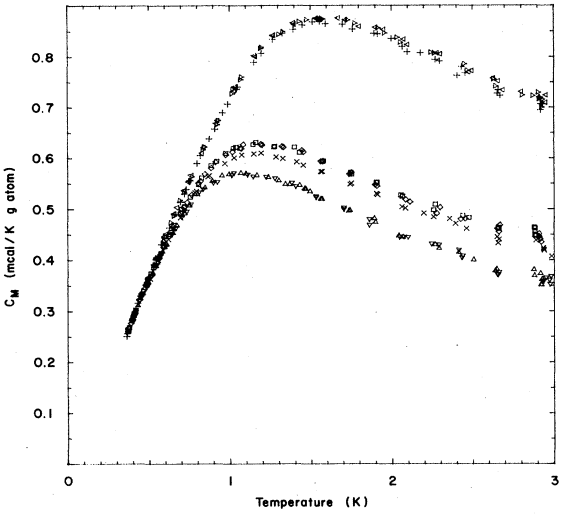

FIG. 3. Magnetic contribution to the specific heat for the nominal 0.075 at. % Mn samples. The symbol key is given in Table III.

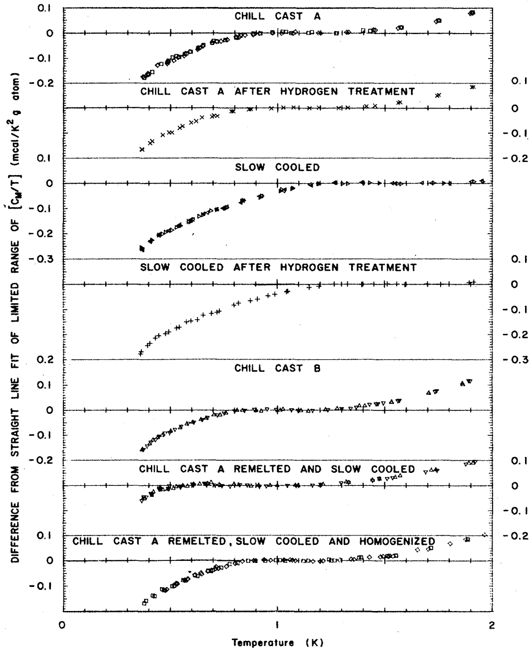

FIG. 5. Deviation of the magnetic specific heat divided by temperature for the nominal 0.075 at. % Mn samples from limited-range straight-line fits. This illustrates the "knee" at the spin-glass freezing temperature. For further details see the text.

tent increases. If, instead, the magnetic specific heat divided by temperature is plotted (Fig. 4) it will be noted that there is a sudden breakaway from the ascending linear region and, for the results on the 0.083 at. % Mn alloy reported previously,^{6} the temperature of this "knee" in the curve corresponds to the spin-glass freezing temperature (T_f). The "knee" is made more obvious by fitting the linear ascending region of each curve to a straight line and plotting deviations from this line [in units of magnetic (specific heat)/(temperature)], see Fig. 5. It will be observed that the "knee" temperature is around 1.2 K for the slow-cooled sample 0.9 K for chill-cast A, and 0.8 K for chill-cast B.

The experiment in which the chill-cast A sample (after hydrogen treatment) (×) was melted and slow cooled (△▽) and then homogenized for 66 days (□◇) is illustrated in Fig. 6. It will be observed that the "knee" for the slow-cooled, unhomogenized state is at a lower temperature than found for the other states and that the "knee" may be at a slightly lower temperature for the slow-cooled and homogenized state than for the original chill-cast, homogenized, and hydrogen-treated state (see also Fig. 5). The integrated area under the plot of Fig. 6 is the entropy. Thus, the entropy increases less rapidly for

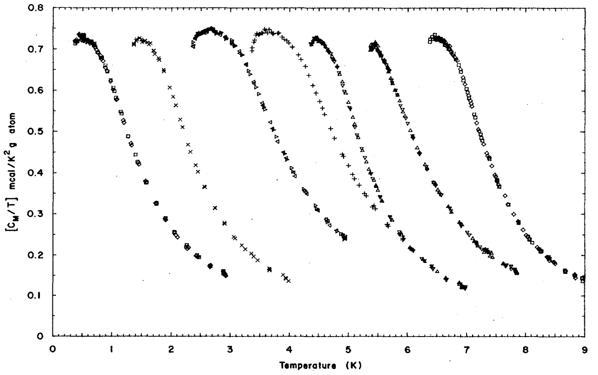

FIG. 4. Plot of magnetic specific heat divided by temperature against temperature for the nominal 0.075 at. % Mn samples. The symbol key is given in Table III. Results are plotted left to right in the order listed in that table and, for clarity, each curve other than the first is displaced by a multiple of 1 K.

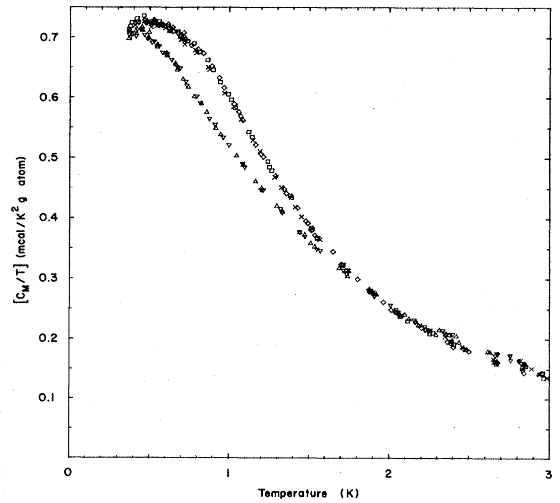

FIG. 6. Plot of magnetic specific heat divided by temperature against temperature for the sample chill cast A after homogenization (×), after remelting and slow cooling (△,▽), and after further homogenization (□,◇).

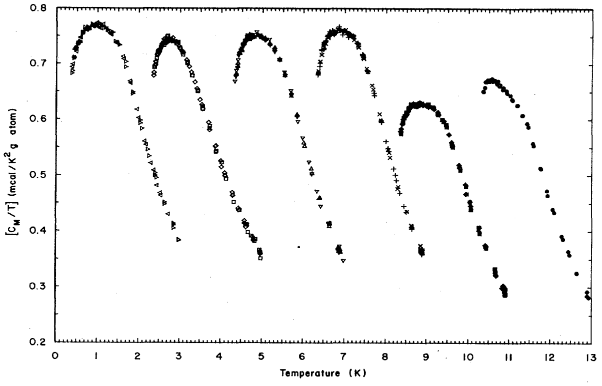

FIG. 7. Plot of magnetic specific heat divided by temperature, against temperature for the 0.083 at. % Mn sample. Symbol key: in original state (chill cast and homogenized) ◁ ▷, after remelting and slow cooling □◇, after 1 day homogenization △▽, after 7 days homogenization + ×, after 30 days homogenization (accidentally oxidized) ■◆, and after hydrogen treatment ●. For clarity all curves, except the first, are displaced by a multiple of 2 K.

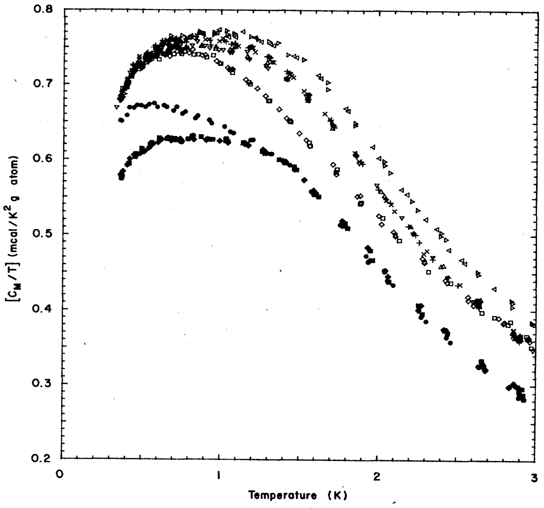

FIG. 8. Plot of magnetic specific heat divided by temperature against temperature for the 0.083 at. % Mn sample. The data are the same as illustrated in Fig. 7 but all are plotted on the same temperature scale.

the slow-cooled, unhomogenized, state than for the others but it will be observed that the curves cross at around 2 K when the rate of increase of entropy with temperature apparently becomes greater for the least homogeneous state. Owing to the shape of the phase diagram, slow cooling is expected to result in relatively large composition gradients in the sample. Since the temperature of the "knee" (and possibly T_f) is depressed under these conditions, it could be that T_f for an inhomogeneous sample is determined by the composition of the region of smallest Mn content.

The 0.083 at. % Mn chill-cast and homogenized alloy, for which results had been published previously,[6] was remeasured (◁ ▷), melted, and slow cooled (□◇), homogenized for 1 day (△▽), then 7 more days (+ ×), and finally 33 more days (■◆) with results as shown in the magnetic specific-heat divided by temperature plots in Figs. 7 and 8. Deviations from a straight-line fit to the linear region are given in Fig. 9. As detailed above, the first (one-day) homogenization was done incorrectly. This resulted in considerable Mn loss and the results after the one- and seven-day homogenizations were lower than for the original state. There was a significant difference in the region of the maximum (Fig. 8) between the results of the one- and eight-day (total) homogenizations. This could indicate that in one day homogenization was incomplete or it could be that Mn evaporation during the one-day homogenization (see above) resulted in a concentration gradient within the sample. As mentioned in the previous section, the sample was partly oxidized during the degassing following the 33-day homogenization, owing to a crack in a quartz tube. The results (■◆, Fig. 8) are interesting because the magnitude of the magnetic specific heat is considerably reduced (by nearly 20%) but the position of the "knee" is little affected (Fig. 9). This suggests that only the outer part of the sample was affected by the oxidation and the remaining 80% retained an effective Mn contribution close to that remaining after the one-day homogenization. The results after the attempt at reduction in hydrogen and subsequent degassing (●, Fig. 8) show a significant increase at the lower temperatures and possibly a slight decrease at the highest temperatures. This probably confirms the oxidation hypothesis but also shows the difficulty in reducing the oxide when once formed.

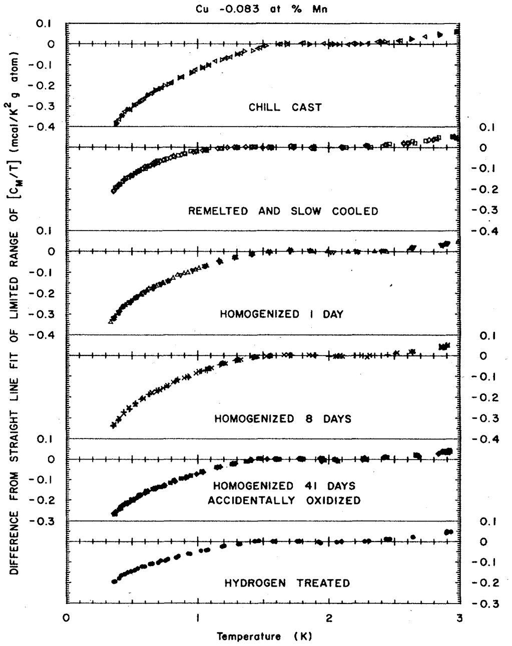

FIG. 9. Deviation of the magnetic specific heat divided by temperature for the 0.083 at. % Mn samples from limited-range straight-line fits. This illustrates the "knee" at the spin-glass freezing temperature. For further details see the text.

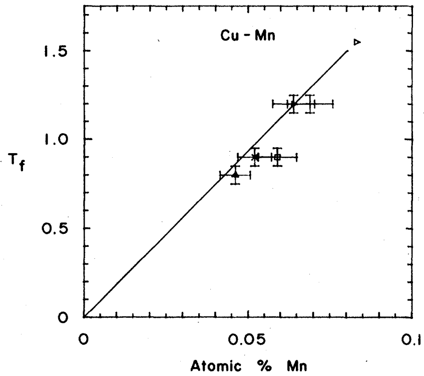

FIG. 10. Plot of "temperature of low-temperature deviation from straight-line plot" (for well-homogenized samples) vs composition as determined from chemical analysis.

If we assume that the composition of the 0.083 at. % Mn sample was accurately known in its original state, then the spin-glass freezing temperatures of more dilute alloys, as a function of composition, should fall on a straight line joining the 0.083 at. % Mn result to the origin. (T_f is almost proportional to composition in this dilute range.[11]) Figure 10 is such a plot for the well-homogenized alloys as a function of the chemical analysis result for the Mn composition. If we assume that the "knee" position is determined within ±0.05 K and that the chemical analysis result for Mn is correct to ±10%, then the hypothesis that the "knee" coincides with the spin-glass freezing temperature (T_f) appears reasonable. Clearly it would be of interest to make low-field susceptibility measurements on similar alloy samples to see whether the temperature of the susceptibility cusp is affected by the degree of homogeneity.

While there are several other publications on the specific heat of Cu-Mn alloys, the only work directly comparable to the present data is that of Fogle *et al.*[8] who present results for a Cu-0.279 at. % Mn alloy in both zero and nonzero magnetic fields. Considering only the zero-field data, their results show a rapid fall of $d(C_M/T)/dT$ as temperature is increased in the region of T_f with relatively steady values of $d(C_M/T)/dT$ immediately above and below this fall. The result is therefore similar to those presented in the present work but the "knee" is more rounded, as measurements in this laboratory for more concentrated alloys have shown.[5] (As the alloy concentration increases the random nature of the solid solution will be perturbed by chemical clustering of the Mn atoms[9] and sharp effects may be rounded owing to local inhomogeneity.) In a later paper Fogle *et al.*[12] further analyzed their results, and by making assumptions about the background specific heat, concluded that there was a small specific-heat anomaly in the region of T_f but the entropy associated with this anomaly was only a tiny part of the total magnetic entropy. Further, the magnitude of this anomaly decreased with increasing magnetic field. Fogle *et al.* find some agreement between their results and mean-field theory. However, their result (and ours) appears to contradict the conclusion of Berton *et al.*,[13] deduced from results on the magnetocaloric effect, that "it is hopeless to look for singularities in the specific-heat measurements at strictly zero magnetic field in the region of T_f." It may be concluded that recent zero-field specific-heat measurements on Cu-Mn alloys in the region of T_f show that there is a subtle effect in the specific heat here, which may become sharper as the Mn concentration is reduced. Comparing these results with Ehrenfest's classification[14] it might be deduced that if there is a "transition" at T_f it is of a third or fourth order, depending on the sharpness of the "knee."

The present results alone do not answer the question of whether the changes in various properties occurring at the spin-glass freezing temperature T_f are the result of a true phase transition or whether they are the consequence of a dynamic nonequilibrium process. However, both experimental and theoretical results appear to be moving in a direction to support the true phase transition. A list of these experiments is given by Kinzel and Binder[15] who explore, by Monte Carlo simulation, the possibility of a nonzero value of T_f in two dimensions. Using the same technique, Young[16] shows that a finite value of T_f is possible in three dimensions. In comparing theory and experiment the problem will be to reconcile the idealized theoretical model with the imperfections of the experimental sample and results.

Apart from the detailed question of what happens in the region of T_f, the specific-heat results show that about half the magnetic entropy is found above T_f. Thus, the specific-heat results could support a model in which clusters gradually form well above T_f and extend in total volume as the sample cools until at T_f they percolate into a frozen infinite cluster. The remaining spins become incorporated into this infinite cluster as the temperature is further reduced. A system of this type has been discussed by Mydosh,[9] following earlier proposals by others.

CONCLUSIONS

The results presented here support an earlier suggestion that a "knee" in a plot of (C_M/T) against T occurs at the spin-glass freezing temperature T_f. Secondly, the specific heat in the region of T_f is drastically affected by the degree of homogenization of the sample. Thirdly, the results show how easily the effective Mn content of an alloy can be altered by evaporation and oxidation.

ACKNOWLEDGMENTS

I am indebted to J. W. Fisher for preparing and heat treating the alloys, and to several members of the Analytical Chemistry Section for the analysis results, in particular to Dr. S. Berman and Dr. J. W. McLaren for discussions regarding the Mn composition determinations.

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