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Specific heat of dilute Au-Fe and Cu-Mn spin-glass alloys below 30 K

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Specific-heat measurements in the 0.35–30-K temperature range are reported. Annealed Au-Fe alloys containing approximately 0.5 and 2.0 at. % Fe were measured and the latter alloy was also measured after quenching. The main findings confirm those published previously for a 1-at. % Fe alloy. Single-crystal Cu–0.32 at. % Mn was measured and was then melted and homogenized, and measurements on the resulting polycrystalline sample (Cu–0.29_5 at. % Mn) were made in the 2–30-K range. There is probably no difference between the specific heats of single-crystal and polycrystalline materials of the same composition. The paper includes some information on the Cu-Mn phase diagram at 1 at. % Mn and below. Results for both Au-Fe and Cu-Mn confirm the previous observation that the rate of increase of magnetic entropy with temperature shows a sudden decrease in the region of the spin-glass freezing temperature (where a cusp is observed in the magnetic susceptibility) consistent with a higher-order phase transition here.

INTRODUCTION

The observation[1] of the cusp in the magnetic susceptibility of various spin-glass alloys [at the so-called spin-glass freezing temperature (T_f)] led to a great deal of experimental and theoretical work (for recent reviews see Refs. 2 and 3). A number of theoretical results predicted a cusp, or other anomaly, in the magnetic specific heat (C_m) at T_f but this has never been observed. The present author observed[4] a "knee" at T_f in a plot of C_m/T versus T for a dilute Cu-Mn alloy and, some years ago, measured a single Au-Fe alloy (1 at. % Fe) showing a similar effect.[5] (The term "knee" is used to indicate a change of slope which may occur over a small temperature range rather than suddenly.) Since then similar results have been obtained for other Cu-Mn alloys[6,7] and the present paper now presents results for two other Au-Fe alloys. Phillips and co-workers[8] have seen similar effects but have interpreted them differently.

Two recent independent experiments[7,9] have been concerned with the effect of sample perfection on specific heat results. In both cases homogenization of the sample (by means of high temperature heat treatment) resulted in rather large changes of specific heat in the region of T_f. This raised the question whether the specific heat of a single crystal would differ from that of a polycrystalline sample and hence the present work on Cu-Mn was undertaken.

Owing to the much higher lattice specific heat of gold at low temperatures compared with that of copper, the magnetic contribution to specific heat is a much smaller part of the total in Au-Fe alloys than in Cu-Mn alloys. Hence the results for Au-Fe alloys are less clear cut than those for Cu-Mn alloys. However, they are consistent with a "knee" in C_m/T in the region of T_f.

EXPERIMENT

The Au-Fe alloys were made from the same starting materials and in the same general way as described earlier,[5] i.e., induction melt in a reducing hydrogen atmosphere, chill-cast under vacuum, homogenize in a hydrogen atmosphere, and degas by heating under vacuum. However, there were differences in detail. In the case of the Au–0.5-at. % Fe alloy a mechanical pump failure during the final degassing resulted in a poor vacuum and possible oxidation. A similar problem with a Cu-Mn alloy[7] had shown that it was not easy to reduce any oxide by hydrogen treatment of the solid at high temperatures. In view of the value of the sample, it was decided to remelt in a hydrogen atmosphere and then chill cast still in hydrogen in order to expose a very large area of molten material to hydrogen. After this was done the sample was remelted under hydrogen and chill-cast under vacuum, and so on as described above. The Au–2 at. % Fe sample was prepared as described above but the starting material was the Au–1 at. % Fe sample, used earlier,[5] with added Fe. The iron content of the alloys was determined by the inductively coupled plasma atomic-emission spectroscopy (ICP-AES) method. Pieces were taken from each end of each sample for analysis. For the nominal 0.5-at. % Fe alloy the results were 0.13±0.01 and 0.14±0.01 wt. % Fe giving 0.47_5 at. % Fe as an average and an average atomic weight 196.30. A mass spectrometer analysis showed the following major impurities (at. ppm) C, 10; O, 6; Al, 10; Cu, 10; Ag, 20. All other impurities were less than 1 ppm. For the nominal 2.0 at. % Fe alloy the ICP-AES result was 0.55±0.01 and 0.56±0.01 wt. % Fe leading to 1.93 at. % Fe average and an average atomic weight of 194.24. Major impurities were Cu, 2; and Ag, 8 ppm. All other impurities were less than 1 ppm. The 0.5 at. % Fe sample weighed 73.67 g and the 2 at. % Fe sample was 82.13 g.

After the specific-heat measurements were completed, small cylinders were cut from each sample for magnetic susceptibility measurements.[10] A cylinder had also been taken from the 1 at. % Fe sample, measured earlier,[5] before it was destroyed. The remaining part of the 2 at. % Fe sample was then cleaned and sealed, resting on an alumina support, in a quartz tube under vacuum. The sample was heated to 850 °C for about 18 h and quenched into brine at −7 °C and installed in the 3–30-K calorimeter, cooling beginning 3 h after the quench. A single specific heat run was then made on this "quenched" sample which weighed 72.40 g.

After the magnetic measurements were finished the small cylindrical samples were independently analyzed for iron[10] by the atomic absorption method with the following results. (National Research Council values, quoted above, are in parentheses.) Nominal 0.5 at. % Fe alloy, $0.50_8 \pm 0.005$ ($0.47_5 \pm 0.035$); nominal 1.0 at. % Fe alloy, $1.03_8 \pm 0.01$ ($1.03_3 \pm 0.035$);[5] and nominal 2.0 at. Fe alloy, $2.06_3 \pm 0.02$ (1.93 ± 0.04). In view of these results the composition of the alloys will be taken to be the nominal compositions. As far as the specific heat results are concerned, any error in composition affects the average value taken for the "atomic weight" of the alloy and hence the specific heat expressed per gram-atom, the possible errors of ±0.05% or less being much smaller than the scatter of results and therefore considered negligible.

One problem in growing an alloy single crystal arises from the shape of the phase diagram,[11] i.e., the compositions of the solid and liquid in equilibrium are different. In an attempt to minimize this problem the mass of the initial melt (~240 g) was made considerably greater than the mass of the crystal grown (~80 g). The starting materials, 99.999% pure American Smelting and Refining Co. (ASARCO) copper and hydrogen-treated high-purity electrolytic flake manganese from MacKay, were inductively melted, under an argon atmosphere, in an alumina crucible surrounded by a graphite crucible used as a susceptor. The crystals were grown from a pure copper seed using the Czochralski method with a pulling spread of about 2 cm/h. The original intention had been to grow an approximately 2-cm-diam crystal from a 1 at. % Mn melt and samples with an initial composition of about 0.8 at. % Mn were obtained, but it was not possible to obtain a single crystal. (A recent reference[12] suggests that a much slower growing speed would have been advisable.) Reasonable success was obtained with approximately 1 cm diam crystals from 0.5 at. % Mn melts. The ends were spark cut off two such crystals and the large remaining sections were heat treated for 36 days at 1000 °C, while resting on alumina inside a sealed quartz tube containing hydrogen, in order to remove microsegregation. The crystals were then transferred to a degassing apparatus where they were heated slowly to around 890 °C under continuous pumping. (This was to remove hydrogen gas which may result in large specific heat anomalies at low temperature.[7]) There was some deposit on the tube of the degassing apparatus and it was suspected that some Mn had evaporated. The crystal weights were therefore reduced by about 5% by etching in order to remove the surface layers.

Disks were then spark cut from the center and ends of each crystal for chemical analysis. A manganese determination was made by the ICP-AES method. For both crystals the first grown disk was reported to contain 0.27% Mn wt./wt., whereas the other two disks were 0.28% Mn wt./wt. Thus one section from each crystal was 0.28% Mn wt./wt. and both of these pieces were used for the specific heat measurements, giving a sample of weight 49.774 g, of composition 0.32 at. % Mn, and "average" atomic weight 63.512. Careful inspection of these pieces showed a few tiny crystals of different orientation in the surface but it is believed that these imperfections represented less than 1% of the total. It is also probable that the pieces had a linear concentration gradient, but less than the 0.01 at. % Mn set by the precision of the analysis results. As noted above there might also be a radial composition gradient. A mass spectrometer analysis was also run on each of the disks mentioned above. From these data the following impurity analysis is obtained for the specific-heat sample material: Al, Si, P, S, Ni, Ag, Sn, and W all less than 1 ppm atomic, Fe 4 ppm atomic. Thus the impurity content should have a negligible effect on the results.

In order to make the most direct comparison possible between the single crystal results and polycrystalline material it was decided to make a polycrystalline sample from the single crystal sample. After the specific-heat measurements were completed the sample was inductively melted, under vacuum, in an alumina crucible and allowed to resolidify in the crucible. It was then homogenized 30 days at 1000 °C while resting on alumina inside a sealed quartz tube containing hydrogen, and then degassed as described above but taking care to minimize the time at a high temperature. (See Ref. 7 for a demonstration of the effect of homogenization.) After the specific-heat measurements were made on this sample, pieces were removed from top and bottom for composition determination by the ICP-AES method. The results were 0.25 and 0.26% Mn wt./wt., giving an average composition of 0.29_5 at. % Mn and indicating some loss of Mn during the remelting and subsequent heat treatment. In retrospect, a better way to prepare the polycrystalline sample might have been to cold work the single crystal material.

The specific-heat measurements were made in the two different calorimetric apparatuses[4,6] used in previous work and covering the temperature ranges 0.35–3 and 2.5–30 K, respectively. The ambient magnetic field outside the cryostat was about 0.03 mT, sometimes increasing to 0.06 mT owing to use of a high field magnet in a neighboring laboratory. This variation had no significant effect on the specific heat.

RESULTS

Two runs, with intermediate warm to room temperature, were made in each of the two apparatuses used on both annealed Au-Fe samples. After quenching, a single run was made on the Au–2 at. % Fe sample in the higher temperature apparatus. The magnetic specific heat was obtained, as described earlier,[5] by subtracting the specific heat of pure gold from the alloy results. (The nuclear specific heat of Fe is negligible in this temperature range.[5]) The magnetic specific heat is plotted as a function of temperature in Fig. 1 and (magnetic specific heat)/temperature versus temperature in Fig. 2. Part of Fig. 2 is reproduced in Fig. 3 which also includes the earlier results[5] on a 1 at. % Fe alloy. Error bars show the magnitude of 1% or 0.1% of the specific heat of pure gold.

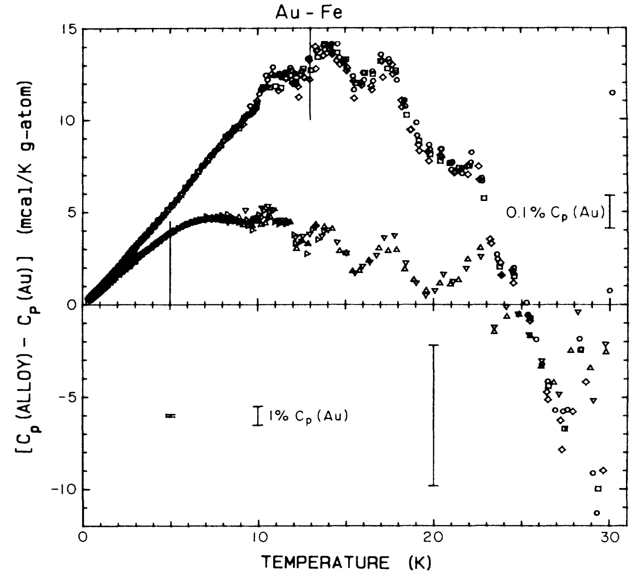

FIG. 1. Plot of magnetic specific heat vs temperature for Au-Fe. The upper curve is the 2 at. % Fe sample and the results after quenching are shown by ○. The lower curve is the 0.5 at. % Fe sample. The error bars indicate the magnitude of the specific heat of pure gold while the vertical bars, intersecting the data, are the T_f temperatures as determined from magnetic susceptibility measurements on the same material.

The dc magnetic susceptibility of cylinders cut from the specific-heat samples was measured elsewhere[10] (on field cooled samples in a field of 1 mT) and the T_f temperatures obtained (5.0, 8.5, and 13 K for the 0.5, 1, and 2 at. % Fe samples, respectively) are indicated by vertical bars in Figs. 1, 2, and 3.

Four runs, as detailed above, were made on the Cu-Mn

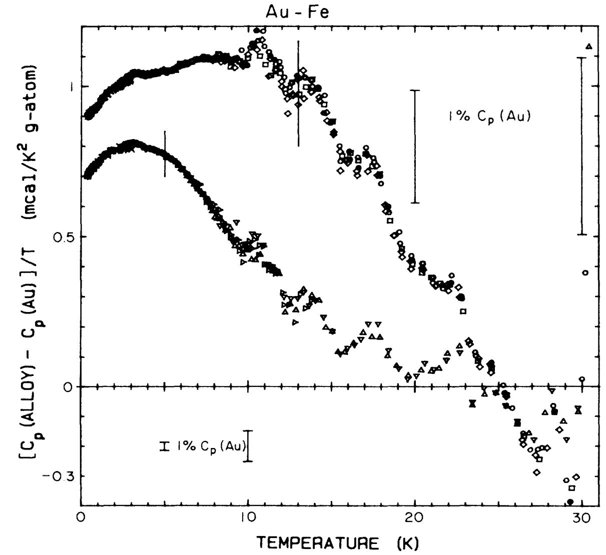

FIG. 2 Plot of (magnetic specific heat)/temperature vs temperature for Au-Fe. Details as in the legend to Fig. 1.

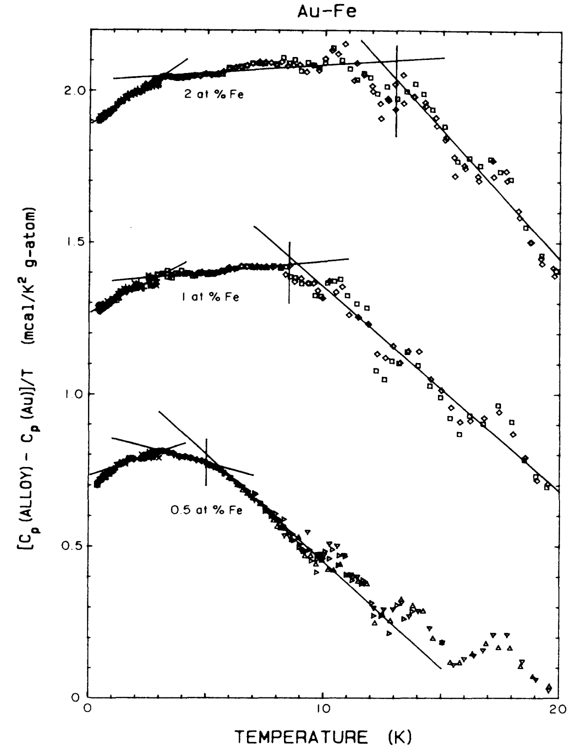

FIG. 3. Plot of (magnetic specific heat)/temperature vs temperature for Au-Fe. Also included are results on a 1 at. % Fe alloy from Ref. 5. For clarity the 1 at. % Fe results are displaced upwards by 0.5 mcal/K g-at. and the 2 at. % Fe results are displaced upwards by 1.0 mcal/K g-at. For a discussion of the fitted lines see text.

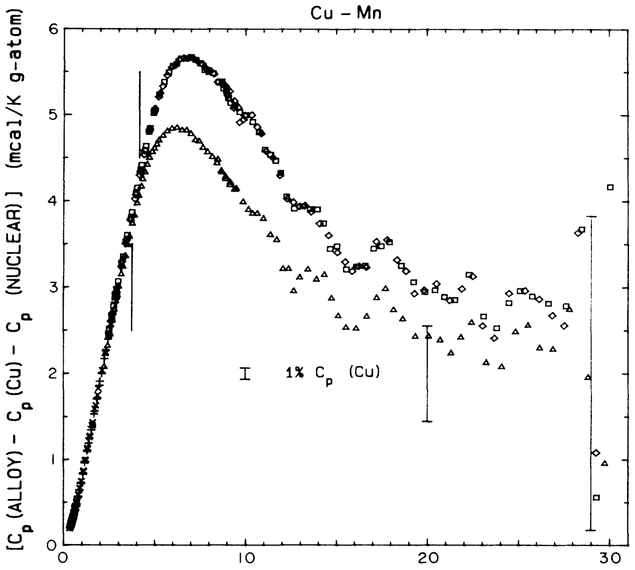

FIG. 4. Magnetic contribution to the specific heat for Cu-Mn. Results for the polycrystalline sample are indicated by △; all other symbols refer to the single-crystal sample. The vertical lines indicate the T_f temperatures and the error bars show the magnitude of 1% of the C_p of pure copper.

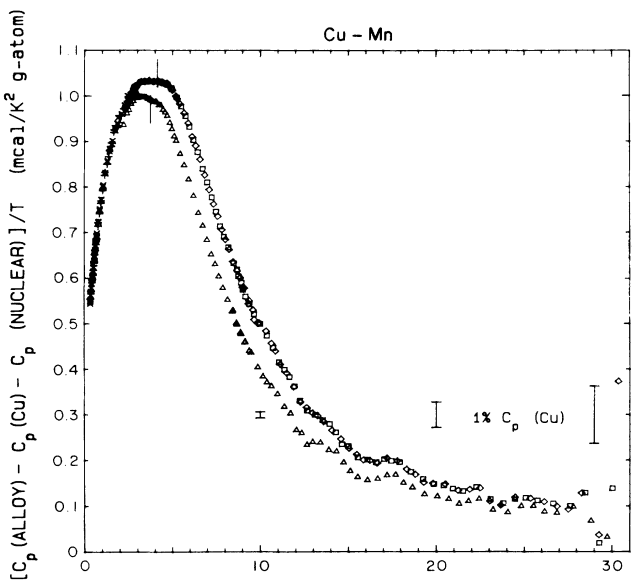

FIG. 5. Plot of magnetic specific heat divided by temperature against temperature for Cu-Mn. Symbols and other information as in Fig. 4.

single crystal. The specific heat of pure copper[6] and an estimated nuclear contribution[4] from the Mn were subtracted from the alloy results and the magnetic specific heat (C_m) is plotted in Fig. 4. (The validity of this subtraction procedure has been discussed elsewhere.[6]) Figure 5 shows a plot of (C_m/T) versus temperature and Fig. 6 is an enlargement of part of the plot showing least squares fits of straight lines in the regions 3 to 4.5 and 5.5 to 8.5 K.

A single run was made on the polycrystalline sample prepared from the single crystal sample. The results were evaluated as above and are shown in Figs. 4 to 6 as outlined above, the straight lines in Fig. 6 being fits in the regions 3 to 4.4 and 5 to 8 K, respectively.

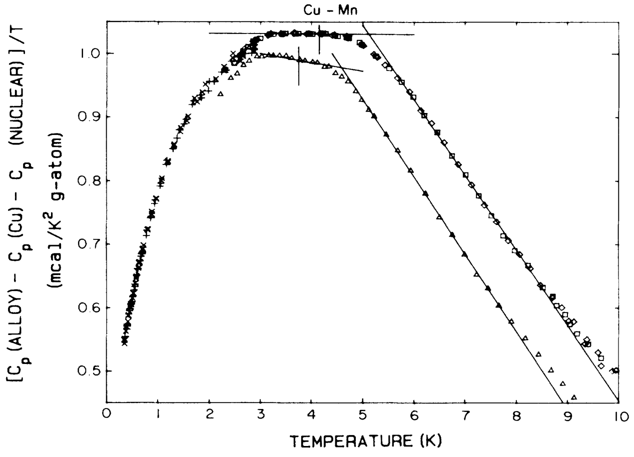

FIG. 6. Detail of part of Fig. 5 with least-squares-fitted straight lines (see text). Symbols and other information as in Fig. 4.

A small cube was spark cut from the unused part of one of the single crystals, next to the slice analyzed as 0.27% Mn wt./wt. The T_f as determined[10] from dc magnetic susceptibility measurements on a field cooled sample in a field of 1 mT was 4.0_0 K, falling exactly on a plot of T_f versus composition determined for polycrystalline samples. An independent composition determination[10] agreed exactly with the value already given. From the susceptibility results it is estimated[10] that T_f for the single crystal specific-heat sample is 4.1_5 K and for the polycrystalline sample T_f is 3.7_5 K.

DISCUSSION

Results for the Au-Fe samples will be discussed first. It will be obvious from Figs. 1 and 2 that quenching has had little or no effect on the specific heat of the 2 at. % Fe sample. This result was not unexpected; see the discussion on quenching in Ref. 5.

The plot of magnetic specific heat against temperature (Fig. 1) shows that maxima of the anomalies occur at higher temperatures than the "freezing temperatures" (T_f) indicated by vertical bars intersecting the data. The approximately linear regions on the low-temperature side of the maxima show a small positive intercept on the temperature scale rather than being proportional to absolute temperature. The data become negative above about 25 K. This is undoubtedly a lattice dynamics effect. The Fe atoms are much lighter than the Au atoms resulting in high frequency impurity modes with consequent depletion of the low-frequency end of the spectrum. The scatter of the data in Fig. 1 becomes quite bad above about 9 K. This is because the magnetic specific heat becomes only a small part of the total and, because the subtracted specific heat of pure gold was represented by a smoothed function, deviations owing to temperature scale errors are magnified. For the same reason the plot of (magnetic specific heat)/temperature versus temperature (Fig. 2) is not as clear as one would wish. Part of this plot is reproduced in Fig. 3 which also includes the raw data from the earlier results on Au–1 at. % Fe. The vertical bars intersecting the data are T_f values determined from magnetic susceptibility data.[10] The straight lines illustrated were obtained by least-squares fits of data in the following, rather arbitrary, temperature ranges: (a) for Au–2 at. % Fe: 0–3, 3–12, and 14–25 K; (b) for Au–1 at. % Fe: 0–3, 3–8, and 10–20 K; (c) for Au–0.5 at. % Fe: 1–3, 3–4.5, and 6–8 K. The intercept temperatures are 3.08 and 12.32 K for the 2 at. % Fe alloy, 2.96 and 8.83 K for the 1 at. % Fe alloy, and 3.10 and 5.54 K for the 0.5 at. % Fe alloy. The lower-temperature intercept (at about 3 K) is undoubtedly related to the temperature scale since it is the same for all three alloys. (Compare with the feature at 17.5 K.) The higher temperature intercept is in the region of T_f for all three alloys. The value obtained for this intercept depends on the ranges chosen for the straight line fits. The least ambiguous is the 1 at. % Fe alloy where the intercept is at 8.83 K, comparing well with the measured[10] T_f of 8.5 K. Considerable latitude is possible for the 2 at. % Fe alloy but the specific-heat results are not inconsistent with the measured T_f value. For the 0.5 at. % Fe alloy the scatter of results above about 9 K made it difficult to get a good fit with the less scattered data below. For this reason a short fitting range was used but it is probable that the fitted line is overly steep. However, it is clear from Fig. 4 that there is a "knee" in the region of T_f for all three alloys. The term "knee" is used, as opposed to "discontinuity," to indicate that the change of slope may occur over a small temperature region near T_f rather than suddenly at T_f.

Turning now to the Cu-Mn results it will be seen that the C_m plot for the remelted (polycrystalline) sample (Fig. 4) is the same shape as for the single crystal but the maximum value of C_m is less and the temperature of the maximum is displaced to a lower temperature, both facts consistent with a loss of Mn. As previously observed[4] the linear portion (below about 5 K) of the C_m-versus-T plot extrapolates to a positive temperature intercept and the maximum is at a higher temperature than the estimated T_f value. (Thus results for Au-Fe and Cu-Mn show similar features.) The form of the (C_m/T) plot (Figs. 5 and 6) is closely similar for the single crystal and polycrystalline samples. Another similarity is that the T_f value for the single crystal sample falls on a plot of T_f versus composition obtained for polycrystalline samples.[10] The T_f for the Cu–0.32 at. % Mn single crystal was estimated to be 4.1_5 K from magnetic measurements.[10] Rather arbitrary straight lines are fitted in Fig. 4 and intercept at 5.12 K for the single crystal results. It will be observed that the rounded "knee" begins near the measured T_f value. For the less homogeneous polycrystalline sample the lines intersect at 4.58 K but the region of best fit for the lower temperature line is less clear and it could equally well be more horizontal when the intercept temperature would be reduced and the rounded "knee" would again begin near the measured T_f value. This correlation between T_f and the start of the fall in (C_m/T) in the region of the "knee" is also exhibited in Fig. 3 of Ref. 6 for more concentrated Cu-Mn alloys. The present work and Ref. 6 therefore suggest that, for alloys of around 0.5 at. % Mn, the linear fall in (C_m/T) as a function of T_f begins at a temperature above T_f but the precursor of this fall starts near T_f. As the Mn content is decreased perhaps the width of the rounded part of the knee also decreases resulting in the sharper knee then observed.[4,7,9] The change in shape at about 3 K is a temperature scale effect, discussed above.

Results in the present paper confirm the previous observations of a "knee" in the region of T_f in a plot of (C_m/T) versus T. It is not clear at present whether the exact position and shape of this "knee" depend on the alloy system and composition. There have been two interpretations of this "knee." The present author has suggested that it indicates a decrease of (d^2S/dT^2) as the sample is heated past T_f (S is entropy), consistent with a higher order phase change, probably third order in the Ehrenfest classification. (Rounding of the "knee"may be related to sample inhomogeneity.) Fogle[8] and co-workers have suggested that it corresponds to a small specific heat anomaly superimposed on an otherwise smooth variation of magnetic specific heat with temperature. Either interpretation would support the view that the phenomena observed at T_f correspond to a phase transition rather than a rapidly increasing equilibrium time as the temperature is decreased in this region. Note also that a search failed to find equilibrium time effects in the specific heat,[13] thus lending support to the phase-transition hypothesis. The phase transition is from the disordered state to a long-range ordered state where the order is in time rather than space.

Experimental evidence regarding the phase transition controversy has been contradictory. For example, the cusp in the magnetic susceptibility suggested a phase transition but it was later found, in some cases, that the cusp position was dependent on the probing frequency, suggesting equilibrium time effects. Further work[14] suggested an upper limit for the relaxation time and restored confidence in the idea of a collective phase transition. Similarly, the absence of an obvious anomaly in the specific heat argued against a transition but more recent measurements, cited in this paper, have shown rather subtle effects at T_f, suggestive of a phase transition, which are not obvious in the conventional plot of magnetic specific heat versus temperature. Recent work, using other techniques, also supports the phase transition, see, for example, work on muon-spin relaxation.[15] On the theoretical side many results argued against a transition in three dimensions until fairly recently but it now appears that most, if not all, theoreticians find support for a transition in three dimensions. One reason for the change of view is that, owing to developments in computers, numerical simulations can now be done on much larger models. The question remains how well the model corresponds to a real spin-glass alloy. For a recent brief review of the situation and list of references see van Hemmen.[16] See also Singh and Chakravarty,[17] Binder and Young,[18] and Salamon.[19]

The Cu-Mn chemical analysis results suggest that 0.5 at. % Mn in the liquid is in equilibrium with about 0.31 at. % (0.27 wt. %) Mn in the solid and 1 at. % Mn in the liquid is in equilibrium with about 0.8 at. % Mn in the solid. This supplements information presently available on the phase diagram.[11,20]

Finally, the present work suggests that results for an isotropic single crystal do not differ from those of the same composition polycrystal. It would be interesting to make specific-heat measurements on a single crystal of an anisotropic spin glass, such as Zn-Mn, where susceptibility cusps at two different temperatures are obtained from measurements parallel and perpendicular to the c axis.[21]

Note added. K. A. Mirza and J. W. Loram [J. Phys. F **15**, 439 (1985)] have found maxima near T_f in plots of C_m/T versus T for Au-Fe alloys in the range 2–11 at. % Fe. These "maxima" correspond to the feature which has been called a "knee" in the present paper.

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