

Specific heat of spin-glass Au-1 at. % Fe below 30 K

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The spin-glass contribution to the specific heat shows positive curvature at the lowest temperatures, leading to a region linearly dependent on temperature which extrapolates back to a positive temperature intercept. A plot of (spin-glass specific heat divided by temperature) versus temperature shows a "knee" at the spin-glass freezing temperature. These two findings are similar to recent results on the spin-glass CuMn but contrary to previous conclusions on the AuFe system. At the highest temperatures the specific heat of the alloy is less than that of pure gold.

I. INTRODUCTION

Early experimental work on the spin-glass CuMn suggested that, at low temperatures, the spin-glass specific heat C_m was independent of the concentration and linearly proportional to absolute temperature. This finding was supported by the early theoretical work. For a recent brief review see Ref. 1. More recent experimental work¹ showed that the situation is more complicated. There is a region in which C_m is linearly proportional to temperature, but this extrapolates to a positive temperature intercept while the measured specific heat curves away from the extrapolation to approach absolute zero with a lower slope. These results are supported by recent theoretical developments, summarized in Ref. 1.

The other "classical" spin glass^{2,3} is AuFe. Dreyfus, Souletie, Tournier, and Weil⁴ measured a number of AuFe alloys over the 1 to 4 K temperature range. At 1.5 K they found that C_m for an 8 at. % Fe alloy was about double that of an alloy containing 0.2 at. % Fe. Intermediate compositions occupied intermediate positions. They interpreted C_m as being "practically" linearly dependent on absolute temperature. However, careful examination of their results suggests a positive temperature intercept for the extrapolations, as found¹ recently for CuMn. One aim of the present work was therefore to measure a fairly dilute AuFe alloy to lower temperatures to examine the form of C_m in detail.

The discovery of a cusp in the low-field ac magnetic susceptibility and the observation that, for the same alloy and composition, a number of other properties^{3,5} may show changes at the same temperature (T_f), led to the idea of a phase change occurring at the spin-glass freezing temperature T_f . Wenger and Keesom⁶ measured the specific heat of Au-8 at. % Fe and Au-1 at. % Fe alloys over temperature ranges which included T_f but saw no anomaly or other effect at T_f . More recently it has been shown⁷ that, in the case of CuMn alloys, there is a broad "knee" at T_f in

a plot of C_m/T versus temperature T . The present work therefore includes a careful measurement over a wide temperature range including the estimated T_f . For the alloy examined a "knee" was found at T_f , contrary to the result of Ref. 6.

AuFe is a more difficult system to study calorimetrically than is CuMn because the lattice specific heat of pure gold is an order of magnitude greater than that of pure copper. Hence, at higher temperatures, the spin-glass component of the specific heat is a much smaller part of the total. The Kondo temperature of AuFe is also considerably higher³ than that of CuMn but is still sufficiently low (~ 0.1 K) that single-impurity effects should not be significant in the present work. The spin-glass regime extends up to about 15 at. % Fe; at higher concentrations long-range ferromagnetic ordering occurs.

The aim of the present work was to measure a single AuFe alloy to see whether the results were similar to those obtained recently^{1,7} for a number of CuMn alloys. Consideration of the results of previous work^{4,6} on AuFe, and the other factors discussed above, suggested that an Au-1 at. % Fe alloy should be suitable for the present purpose.

II. EXPERIMENTAL

The nominally 1 at. % Fe alloy was made from 99.99% pure gold obtained from the Royal Canadian Mint and Johnson-Matthey electrolytic iron rod. The components were induction melted in a flowing hydrogen atmosphere, chill cast, homogenized and degassed as described elsewhere¹ for CuMn alloys, the only significant difference being that no evaporation was observed during degassing, and the sample was therefore held overnight at a higher temperature, 1123 K, before furnace cooling to room temperature. The sample weighed 77.49 g and was in an annealed state. The specific-heat measurements were made in two apparatuses⁸ covering the 0.35-3 and 2.5-30 K

temperature ranges, respectively. Two sets of measurements were made in each apparatus with an intermediate warming to room temperature.

After the specific-heat measurements on the annealed sample were completed, pieces were taken from each end of the sample for chemical analysis. The results of the impurity analysis for each end were identical and as follows (all ppm by weight): Mg, 0.06–0.6; Mn, 0.03–0.3; Si, 0.3–3; Ni, 0.1–0.9; Al, 0.3–3; Ti, 0.03–0.3; Cu, 0.3–3; and Ag, 1.5–15. The iron content was determined by a flame-atomic-absorption method and was 1.05 (± 0.02)- and 1.01₅ (± 0.02) at. % Fe for the two ends. This leads to an average composition of 1.03₃ (± 0.02) at. % Fe and an "average" atomic weight which is 0.025% below the nominal value of 195.56. This difference is so small that all calculations were performed using the nominal value. (The slight composition shift could have resulted from some evaporation during melting because the vapor pressure of gold exceeds that of iron in this temperature range.)

In order to check whether the results were dependent on sample heat treatment, some further work was done. The cleaned sample, resting in a cleaned alumina crucible, was sealed in a quartz container under vacuum and was held for 18 h at 1123 K before quenching into brine at about 266 K. After washing and drying, the sample, which now weighed 72.37 g, was installed in the 2.5–30 K apparatus, the time interval between the quench and the start of cooling below room temperature being less than three hours. Since the results in this quenched state were indistinguishable from those in the annealed state, only a single run was made. However, the region 5–11 K was measured twice.

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

$$\begin{aligned} a_1 &= +0.933\,983\,20 \times 10^{-3} \\ a_2 &= +0.675\,980\,75 \times 10^{-5} \\ a_3 &= +0.161\,649\,06 \times 10^{-3} \\ a_4 &= -0.263\,316\,11 \times 10^{-4} \\ a_5 &= +0.528\,942\,71 \times 10^{-5} \\ a_6 &= -0.664\,766\,58 \times 10^{-6} \\ a_7 &= +0.566\,002\,76 \times 10^{-7} \\ a_8 &= -0.314\,489\,56 \times 10^{-8} \\ a_9 &= +0.105\,522\,31 \times 10^{-9} \\ a_{10} &= -0.191\,942\,17 \times 10^{-11} \\ a_{11} &= +0.144\,894\,22 \times 10^{-13} \end{aligned}$$

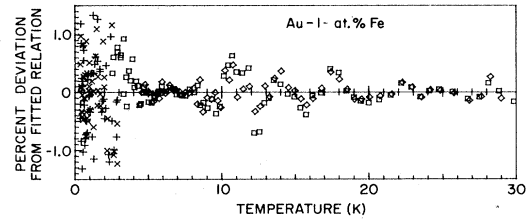


FIG. 1. Deviations of the raw specific-heat data for the annealed sample from the polynomial fit in Table I. The four different symbols refer to the four different experimental runs.

III. RESULTS

Least-squares fits of various polynomials were tried for the combined results of all four experimental runs on the annealed sample. The best fit was the polynomial listed in Table I, and the deviations of the raw data for the annealed sample from this fit are shown in Fig. 1. (The small systematic deviations are associated with small errors in the temperature scale and are similar to those obtained on other materials.⁹) The deviations of the raw data for the quenched sample from the same fit (Table I) are shown in Fig. 2. The heat treatment had no significant effect. There is no evidence for a nuclear term (proportional to T^{-2}) in the specific heat, contrary to the result for CuMn. This is in agreement with earlier work¹⁰ and is because only 2% of the iron atoms have a nuclear spin, and the nuclear contribution to specific heat is therefore very small. (The nuclear contribution becomes visible in the specific heat when measurements are extended to much lower temperatures.¹¹) The spin-glass contribution to specific heat (C_m) (see Figs. 3 and 4) was obtained by subtracting the specific heat of pure gold⁹ from the total specific heat. The validity of this procedure is discussed in Ref. 1 and below.

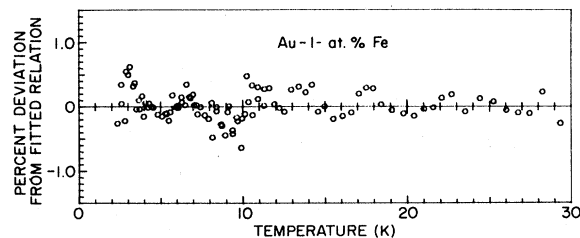


FIG. 2. Deviations of the raw specific-heat data for the quenched sample from the polynomial fit for the annealed sample (Table I).

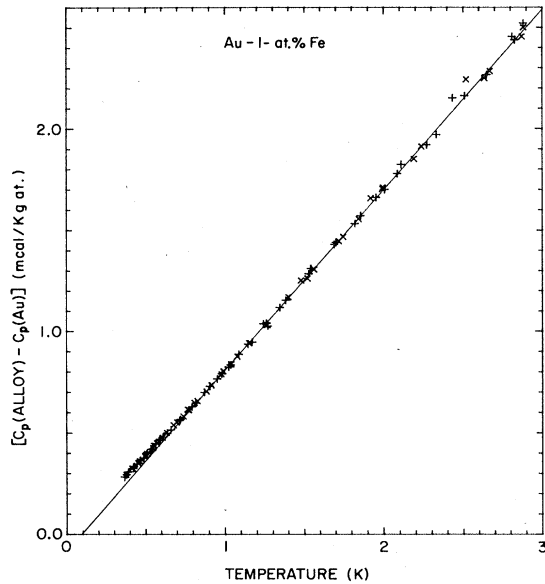


FIG. 3. Plot of the spin-glass specific-heat data for the annealed sample obtained from the lower-temperature apparatus. Note that the linear part extrapolates to a positive temperature intercept.

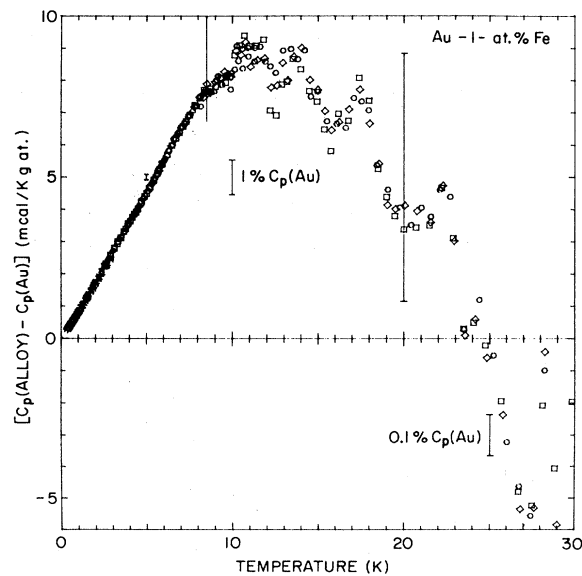


FIG. 4. Plot of all the spin-glass specific-heat data. The vertical bar intersecting the plot is the estimate of T_f for the alloy. The bars in the positive segment of the graph show the magnitude of 1% of the specific heat of gold, while that in the negative segment represents 0.1% of the specific heat of gold. The symbol \circ refers to the quenched sample. The other four symbols are results for the annealed sample.

IV. DISCUSSION

The spin-glass specific heat (sample in the annealed state) obtained with the lower-temperature apparatus is shown in Fig. 3. The least-squares-fitted straight line shows that there is a good linear region which extrapolates to a positive temperature intercept (~ 0.1 K), while the measured points curve away to approach the absolute zero with a lower slope. This behavior is similar to that found¹ for CuMn but, for a given transition-metal concentration, the intercept appears to be an order of magnitude smaller. Recent theoretical work, summarized in Ref. 1, is in agreement with the observed curvature at the lowest temperatures, leading to a linear region at higher temperatures.

The spin-glass specific heat over the whole temperature range of the measurements is shown in Fig. 4. It will be observed that the magnitude of this contribution to specific heat becomes very small compared to the specific heat of pure gold at the higher temperatures and that it apparently becomes negative. This is almost certainly because the lattice-vibration spectrum has been considerably altered on adding light Fe atoms to the gold lattice. The mass ratio is ~ 3.5 and will result in high-frequency impurity modes with consequent depletion of the low-frequency area of the lattice-vibration spectrum.¹² Thus the approximation of subtracting the specific heat of pure gold from that of the alloy to obtain the spin-glass specific heat fails at the higher temperatures but is probably adequate at lower temperatures where the spin-glass specific heat is a much greater part of the total.

There have been a number of measurements of the spin-glass freezing temperature for an Au-1 at. % Fe alloy (summarized by Beck² and Larsen³). The vertical bar intersecting the results in Fig. 4 is at 8.5 K and is the value obtained by Cannella and Mydosh¹³ from the low-field ac-susceptibility cusp. A similar measurement by Werner⁶ gave 8.3 K. It will be observed (Fig. 4) that the maximum of C_m lies at a higher temperature. However, Fig. 5 is a plot of (C_m/T) versus temperature, and it will be seen that there is a broad "knee" at T_f . This correlation is the same as that observed in a number of CuMn alloys.^{1,7} The area under the curve of Fig. 5 is the spin-glass entropy. As discussed in the previous paragraph, there is considerable uncertainty at the highest temperatures. If it is assumed that the plot of Fig. 5 is correct, then the total spin-glass entropy up to ~ 25 K is very close¹⁴ to $R \ln 2$ per g at. Mn with the contributions above and below T_f approximately equal. This total entropy would correspond to spin $J = \frac{1}{2}$ on Mn atoms. From magnetic measurements^{13,15,16} it appears that $J \approx \frac{3}{2}$ for a 1 at. % Fe alloy, and hence the entropy should be about double

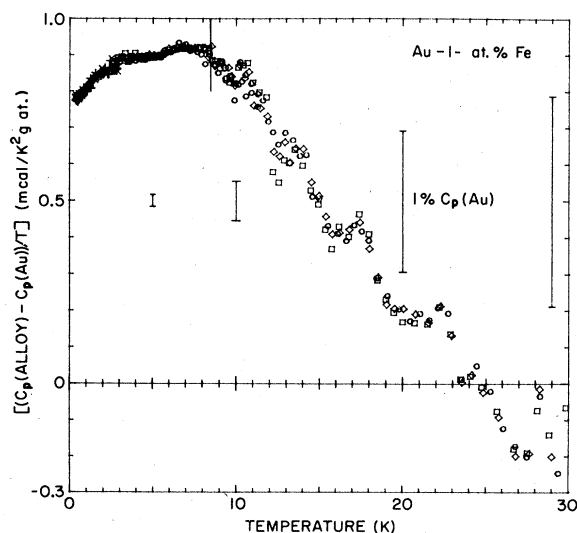


FIG. 5. Plot of (spin-glass specific heat divided by temperature) versus temperature. The vertical bar intersecting the plot is the estimate of T_f for the alloy while the bars show the magnitude of 1% of the specific heat of gold. The symbol \circ refers to the quenched sample. The other four symbols are results for the annealed sample.

that mentioned above. This could be so if the lattice specific heat of the alloy is $\sim 1\%$ less than that of pure gold at the higher temperatures.

The form of the present result in the region of T_f and above is quite different from that of Wenger and Keesom,⁶ who reported an almost constant C_m/T value for an Au-1 at. % Fe alloy up to the limit of their graph (~ 12 K). Wenger and Keesom give no details regarding the preparation of this sample, and hence the homogeneity and thermal history is unknown. However, they do state that it was a single crystal. Experiments on quench-condensed films of AuFe (with Fe ≥ 2 at. %) by Zibold¹⁶ show that T_f and the magnitude and form of the susceptibility effects are dependent on thermal history and that the bulk effects are almost certainly related to clustering of the iron atoms. Experiments on more concentrated bulk samples (cold-working and annealing CuMn and annealing AuFe) lead to a similar conclusion.² However, the present results show no difference between the quenched and annealed state of the rather dilute sample (Figs. 2, 4, and 5). Another possible source of difference between the Wenger and Keesom data⁶ and the present work lies in the value they take for the non-spin-glass specific heat. For the 8 at. % Fe alloy they state that this was calculated from the specific heat of pure gold⁹ in the following way. The ratio (determined at the lowest temperatures) of the Debye temperatures of the alloy and

pure gold was kept constant over the whole measurement range. They admit that this takes no account of possible changes in the lattice-vibration spectrum. However, the procedure also assumes that the spin-glass specific heat is linear in absolute temperature at the lowest temperatures (so that the T^3 term depends only on the lattice specific heat). This assumption is incorrect (Fig. 3). (Furthermore, their lowest temperature of measurement would not be sufficiently low to determine accurately the Debye temperature of pure gold owing to the anomalous variation of lattice specific heat with temperature in pure gold.⁹) It appears that Wenger and Keesom followed a similar procedure with their Au-1 at. % Fe alloy. A detailed comparison of results is not possible because Wenger and Keesom have only presented their data in the form of small graphs.

It is interesting that the present results show no dependence on heat treatment (brine quench and slow cool). There are three possible reasons: (a) A poor quench. This is unlikely since the technique has been used satisfactorily on numerous other alloys. (b) Impossibility of rapidly quenching the whole of the ~ 75 g sample. This is more likely. Experiments on heat treating a Cu-40 at. % Ni sample showed¹⁷ that the cluster concentration could be altered by heat treatment but that it was impossible to suppress clustering. (This is probably related to the enhancement of diffusion resulting from the high equilibrium concentration of lattice vacancies at high quenching temperatures.) Since it is probable that the heat treatment of the present sample would have altered the clustering and no effect was seen in the specific heat, it appears that the effect of any clustering would be small. The final possibility (c) is that clustering is not significant for a bulk Au-1 at. % Fe sample. Thus cold working was found¹⁸ not to affect the susceptibility cusp for a quenched Au-1 at. % Fe sample although it had a marked effect at higher concentrations. Also, a frequency dependence of the temperature of the susceptibility cusp (thought by some authors¹⁹ to be related to clustering) is not seen in dilute AuFe alloys although it occurs in more concentrated alloys.²⁰

As discussed above, both CuMn and AuFe show a region where the low-temperature specific heat is linear in temperature but which extrapolates to a positive temperature intercept while the results bend away to approach the absolute zero with a lower slope. Similar behavior has been reported²¹ for PtMn and the present author's data²² for Zn-0.2 at. % Mn may be reinterpreted in this way. Thus this result may be a general feature for spin glasses which is only now becoming apparent due to more extensive and accurate measurements.

The feature observed in the specific heat of both CuMn and AuFe at T_f is discussed in more detail elsewhere.⁷

CONCLUSION

The present work has shown that the spin-glass specific heat is not linearly dependent on absolute temperature at low temperatures, in agreement with recent results¹ on CuMn and also with some recent theoretical work.¹ Second, as in the case^{1,7} of CuMn, a feature is seen in C_m at T_f . The rate of entropy increase with increasing temperature begins to fall in the region of T_f . T_f as determined from this

specific-heat feature agrees well with that determined from the low-field ac-susceptibility cusp.

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