Magnetic ordering of $Au_{0.92}Fe_{0.08}$: A calorimetric investigation*

L. E. Wenger and P. H. Keesom
Department of Physics, Purdue University, West Lafayette, Indiana 47907
(Received 9 December 1974; revised manuscript received 10 February 1975)

In an attempt to further understand the magnetic ordering found in lower concentration of *Au* Fe alloys, the specific heat of a single crystal of $Au_{0.92}Fe_{0.08}$ was measured in the temperature range 3–50 K. A prior susceptibility measurement on the same sample showed a sharp cusplike peak at 29 K. However, there is no indication of a cooperative-type peak in the specific heat and the magnetic entropy shows only 22% of the iron ions are being ordered between 29 and 0 K. These results appear to be in disagreement with the mictomagnetic description of the susceptiblity and with the existence of cooperative order as originally suggested by the susceptibility result.

INTRODUCTION

This measurement of the low-temperature specific heat of a single-crystal $Au_{0.92}Fe_{0.08}$ sample was a continuation of a low-temperature low-field susceptibility measurement[1] on the same sample. The cusplike peak seen in the susceptibility suggested a magnetic ordering at a well-defined temperature. By extending the temperature range of measurement above the ordering temperature, it was expected that these heat-capacity data would help in characterizing the magnetic ordering in dilute *Au*Fe alloys.

The magnetic and transport properties of alloys containing transition-metal solutes have been studied for many years in the hope that an understanding of the interaction and ordering of magnetic moments would be attained. Two areas were defined from these investigations: the formation and properties of single magnetic impurities, and the interaction between magnetic impurities leading to ordering. These areas and properties of dilute alloys are covered in a review article by van der Berg.[2] More recently, an excellent review article by Phillips[3] summarized the theoretical and experimental results on the heat capacity of dilute alloys.

The main contributions to the heat capacity of dilute alloys are those of the conduction-electron–impurity interactions (Kondo effect) and the impurity-impurity interactions. Since each type of interaction has a characteristic temperature associated with it, the heat capacity of a particular system may be dominated by conduction-electron–impurity interaction in one concentration and temperature region, and by impurity-impurity interaction in another. Typically for impurity-impurity interaction, its magnetic heat capacity at low temperatures is proportional to the temperature and may be independent of the concentration of the solute (e.g., *Cu*Mn[4,5]) or some other nonlinear function of the concentration. Also it has an ordering temperature proportional to the concentration. The magnetic heat capacity associated with conduction-electron–impurity interactions is a single-impurity effect and typically is an anomaly proportional to the concentration (e.g., *Cu*Fe[6]) and is linear in temperature.

The *Au*Fe system is particularly interesting as both single-impurity effects and different types of long-range order are observed in different concentration ranges. For concentrations of iron greater that 12 at.%, long-range ferromagnetic ordering exists. For concentrations less than 12 at.%, high-field magnetization, magnetic remanence, and thermoelectric-power[7–11] results indicate no magnetic transitions but suggest the existence of mictomagnetism. Mictomagnetism is a system characterized by superparamagnetism at high temperatures and a gradual freezing in of the spin orientations when the temperature is lowered. However, magnetic susceptibility,[11,12] Mössbauer,[13–17] and resistivity[18] studies for these concentrations indicate that a magnetic ordering exists with a well-defined ordering temperature T_0, and show a nearly linear concentration dependence of T_0. These studies, the negative values of the paramagnetic Curie temperatures for concentrations of 1–3 at.% and small positive values for 4–8 at.%, and a recent low-field susceptibility investigation[11] showing sharp cusplike peaks at well-defined temperatures (e.g., see Fig. 2) seem to suggest antiferromagnetic ordering for concentrations of iron less than 12 at.%. This susceptibility peak is explained in terms of mictomagnetism[10,19] as an accelerated rate of the freezing in of the superparamagnetic moments at the ordering temperature.

Previous heat-capacity measurements[20–23] on *Au*Fe alloys ($0.092 \leq c \leq 8$ at.%) were undertaken only at temperatures below 4.2 K, well below the ordering temperatures for the higher solute concentrations. These results suggest that impurity-impurity interactions are the dominant effect as the magnetic heat capacity is approximately concentration independent and linear in temperature. The controversy still persists as to the nature of the magnetic order in the concentration region be-

low 12 at.%. Thus the present heat-capacity measurement on a $Au_{0.92}Fe_{0.08}$ sample having the characteristic susceptibility of magnetic ordering was undertaken well beyond its ordering temperature of 29 K to help clarify the existence of the ordering.

EXPERIMENTAL METHOD

The sample, a single crystal of $Au_{0.92}Fe_{0.08}$,[1] was in the form of a bullet and weighed approximately $10\frac{1}{2}$ g. The heat-capacity measurement was made using a standard heat-pulse technique and a ^{3}He cryostat which has been described elsewhere.[24] The addenda included the thermometer, heater wire, glyptal, etc.; and the total addenda heat capacity was measured separately over the same temperature range 3–50 K. A commercially calibrated Ge thermometer[25] was used in this temperature range. The total systematic error is estimated to be less than 1% below 30 K and increasing to a maximum of 2% at the highest tempertures.

The magnetic specific heat is defined as the difference between the measured specific heat and the specific heat of the same alloy as if the impurity atoms were nonmagnetic. With the addition of iron impurities, the increase in the electronic specific heat with respect to pure gold is considered negligibly small. However, a pronounced influence on the lattice specific heat is expected, owing to the large difference in atomic masses of Au and Fe. The lattice specific heat was estimated by calculating the ratio of the measured Debye temperature of this alloy to that of pure Au[26–28] at the lowest temperature, and keeping this ratio constant for all temperatures. This approximation may still leave the magnetic specific heat with substantial error at higher temperatures as it completely neglects the influence of the iron on the shape of the phonon dispersion curves.

RESULTS

The specific heat of the $Au_{0.92}Fe_{0.08}$ sample is shown in Figs. 1 and 2 as plots of C/T vs T^2 as well as that for the calculated nonmagnetic contribution to the specific heat of the alloy. The low-field susceptibility which is shown in the insert of Fig. 2 shows a sharp cusplike peak at a well-defined temperature of 29 K, similar to the results of Cannella and Mydosh.[11] This sharp peak in the susceptibility is suggestive of a material ordering antiferromagnetically near its Néel temperature. Another interpretation is that these transitions correspond to the accelerated freezing in of random spin orientations, similar to the "freezing point" of a spin-glass system.

The low-temperature specific heat shown in Fig. 1 is identical in character with that of other dilute alloys. The magnetic specific heat in the temperature region maintains an approximate linear relationship with the temperature, $C_m = aT$, where $a = 7.1 \pm 0.2$ mJ/(mole of alloy K^2). This value of a is in excellent agreement with previous low-temperature results[21,22] on *Au*Fe alloys.

The linear temperature dependence observed in the magnetic specific heat can be explained by the usual theories[29] of magnetically ordered systems of dilute localized moments. These moments interact through a spatial oscillating coupling of the Ruderman-Kittel-Kasuya-Yoshida type which leads to a molecular-field distribution $p(H, T)$. Various molecular-field models have been proposed and can be successfully applied to describe the temperature dependence of the magnetic specific heat. However, these models do not lead to a sharp cusplike behavior in the susceptibility as seen in the *Au*Fe alloys. The static spin-density wave mechanism[30] for antiferromagnetic order can explain both the linear temperature dependence in the specific heat and the cusplike susceptibility. However, this mechanism predicts a sharp discontinuity in the specific heat at the ordering temperature T_0.

In Fig. 2 the measured specific heat is displayed up to 50 K. Deviations from the low-temperature T^3 law for the lattice specific heat show up quite clearly above 15 K. This is due to the rather low Debye temperature of this alloy ($\Theta_D \approx 167$ K). In the entire temperature range 3–50 K, the specific heat appears to be a monotonic increasing function of the temperature. In contrast, the magnetic specific heat of a system undergoing a cooperative-type ordering is expected to show a λ-type anomaly or at least a discontinuity at the ordering temperature. The measured specific heat around the ordering temperature of 29 K ($T_0^2 = 821$ K^2) shows no indication of an anomaly that could be associated with the onset of cooperative order or the complete

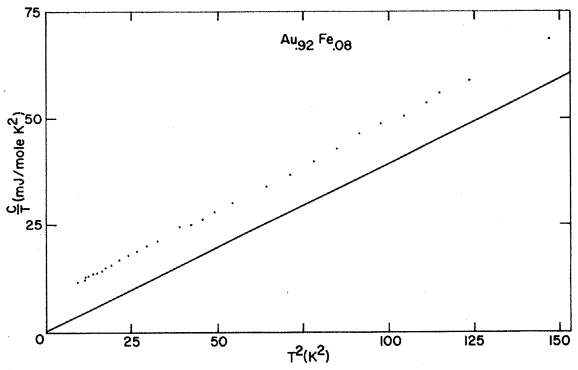

FIG. 1. Specific heat of $Au_{0.92}Fe_{0.08}$ in the low-temperature region is shown as a plot of C/T vs T^2. The solid curve is the calculated nonmagnetic contribution to the specific heat of the alloy.

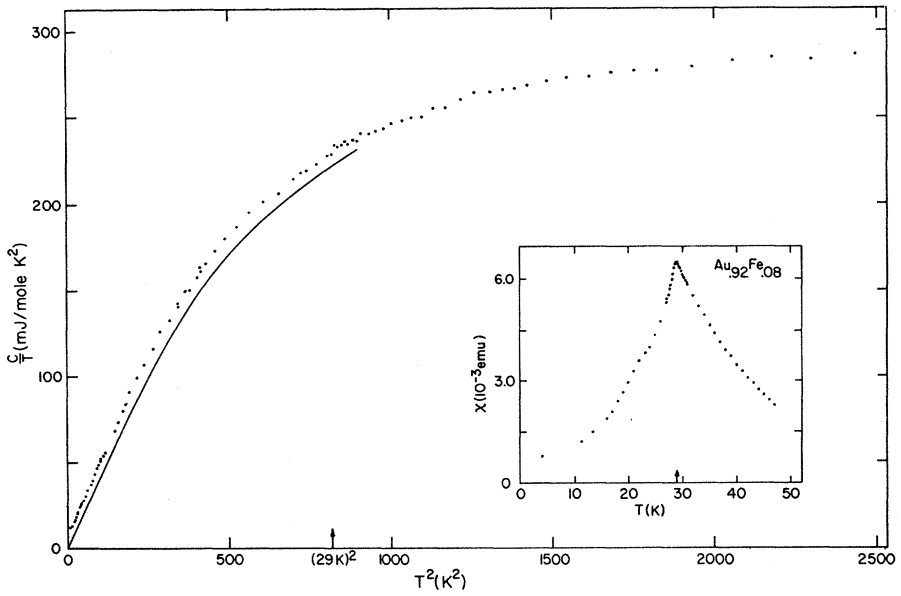

FIG. 2. Specific heat of $Au_{0.92}Fe_{0.08}$ in the temperature region 3–50 K is shown as a plot of C/T vs T^2. The solid curve is the calculated nonmagnetic contribution to the specific heat of the alloy between 0 and 30 K. The insert shows the susceptibility results of the same sample, which were provided by S. A. Werner.

freezing in of the superparamagnetic moments. Taking into account the scatter of the data, an anomaly larger than 20% of the magnetic specific heat should have been readily observable. This corresponds to a change of 1.5 mJ/mole K^2 in the C/T vs T^2 curve.

As a consequence of the small positive value of the Curie temperature ($\Theta_C \approx 4$ K) and of the cusplike susceptibility peak, it could be expected that cooperative magnetic order predominates with short-range order barely noticeable in this sample. Thus it would be expected that the disorder of the magnetic ions would be nearly complete by the ordering temperature of 29 K. Since cooperative ordering of the ions must be complete at absolute zero, the entropy associated with the magnetic specific heat from 0 to 29 K should be nearly equal to $cR\ln(2S+1)$, where c is the concentration of the iron ions, R is the gas constant, and S is the electron spin of the ions. From low-field susceptibility results,[11] the value of the spin S is determined to be 3 for this concentration of 8-at.% Fe. The measured entropy to 29 K is only 0.22 of $cR\ln 7$, so that approximately 22% of the magnetic moments are disordered at the ordering temperature. The entropy measurement is irreconcilable with the assumption that cooperative magnetic ordering is occurring at 29 K in an 8-at.%-Fe sample.

The specific heat and the susceptibility of a single crystal of $Au_{0.99}Fe_{0.01}$ have been measured in the temperature range 2–30 K. These results (see Fig. 3) show similar characteristics as those for $Au_{0.92}Fe_{0.08}$. The cusplike susceptibility peak occurs at 8.3 K, the specific heat shows no indication of a discontinuity nor a cooperative-type peak, and the magnetic entropy from 8.3 to 0 K is only 0.21 of $cR\ln(7)$. The low-temperature magnetic specific-heat contribution can be expressed as $C_m = (3.9 \pm 0.1)T$ in units of mJ/(mole of alloy K), which is in good agreement with previous results.[21,22]

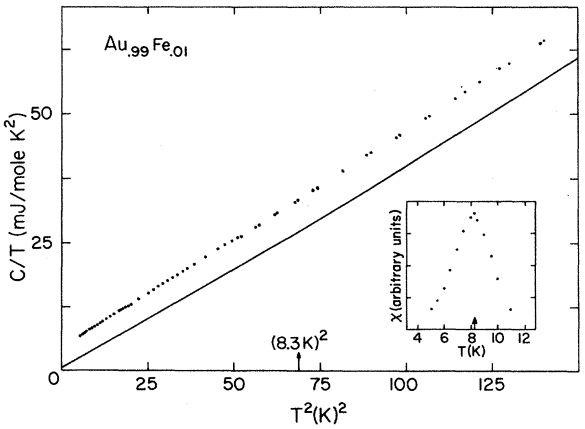

FIG. 3. Specific heat of $Au_{0.99}Fe_{0.01}$ in the temperature region 2–12 K is shown as a plot of C/T vs T^2. The solid curve is the calculated nonmagnetic contribution to the specific heat of the alloy. The insert shows the ac susceptibility results of the same sample.

CONCLUSION

This specific-heat and entropy measurement on $Au_{0.92}Fe_{0.08}$ between 3 and 50 K does not support the assumption of magnetic transitions due to cooperative ordering at well-defined temperatures as originally suggested by the low-field susceptibility and Mössbauer results, nor does it support the mictomagnetism concept used to explain the magnetic and transport properties of the *Au*Fe alloys with solute concentrations below 12 at.%. Further experimental investigations and theoretical developments are necessary in order to understand the mechanisms responsible for all properties of these dilute *Au*Fe alloys.

ACKNOWLEDGMENTS

The authors wish to thank Dr. S.A. Werner for providing us with the sample and its susceptibility results. We are also grateful to Professor A. W. Overhauser for suggesting this investigation and for many informative discussions.

---

*Work supported by the National Science Foundation under Grant No. GH-34731.

[1]The $Au_{0.92}$ $Fe_{0.08}$ sample and its susceptibility measurement were kindly provided by S. A. Werner, Ford Scientific Lab.

[2]G.J. van der Berg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1964), Vol. IV, p. 194.

[3]N. E. Phillips, Crit. Rev. Solid State Sci. 2, 467 (1971).

[4]J. E. Zimmerman and F. E. Hoare, J. Phys. Chem. Solids 17, 52 (1960).

[5]L. T. Crane and J. E. Zimmerman, J. Phys. Chem. Solids 21, 310 (1961).

[6]J. C. F. Brock, J. C. Ho, G. P. Schwartz, and N. E. Phillips, Solid State Commun. 8, 1139 (1970).

[7]W. E. Henry, Phys. Rev. Lett. 11, 468 (1963).

[8]R. Tournier and Y. Ishikawa, Phys. Lett. 11, 280 (1964).

[9]J. Crangle and W. R. Scott, Phys. Rev. Lett. 12, 126 (1964).

[10]B. de Mayo, AIP Conf. Proc. 5, 492 (1972).

[11]V. Cannella and J. A. Mydosh, Phys. Rev. B 6, 4220 (1972).

[12]O. S. Lutes and J. L. Schmit, Phys. Rev. 134, A676 (1964).

[13]R. J. Borg, R. Booth, and C. E. Violet, Phys. Rev. Lett. 11, 464 (1963).

[14]C. E. Violet and R. J. Borg, Phys. Rev. 149, 56 (1966).

[15]V. Gonser, R. W. Grant, C. J. Meecham, A. M. Muir, and H. Wiedersich, J. Appl. Phys. 36, 2124 (1965).

[16]R. J. Borg, Phys. Rev. B 1, 349 (1970).

[17]P. P. Craig and W. A. Steyert, Phys. Rev. Lett. 13, 802 (1964).

[18]J. A. Mydosh, M. P. Kawatra, J. I. Budnick, T. A. Kitchens, and R. J. Borg, in *Proceedings of the Eleventh International Conference on Low Temperature Physics* (St. Andrews University Press, St. Andrews, Scotland, 1969), Vol. 2, p. 1324.

[19]B. de Mayo, J. Phys. Chem. Solids 35, 1525 (1974).

[20]F. J. du Chatenier and A. R. Miedema, Physica 32, 403 (1966).

[21]F. J. du Chatenier, J. de Nobel, and B. M. Boerstoel, Physica 32, 561 (1966).

[22]B. Dreyfus, J. Souletie, R. Tournier, and L. Weil, C. R. Acad. Sci. (Paris) 259, 4266 (1964).

[23]O. Béthoux, Y. Ishikawa, J. Souletie, R. Tournier, and L. Weil, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum, New York, 1965), Vol. B, p. 1023.

[24]G. M. Seidel and P. H. Keesom, Rev. Sci. Instrum. 29, 606 (1958).

[25]Manufactured and calibrated by CryoCal, Inc., Riviera Beach, Fla.

[26]D. L. Martin, Phys. Rev. 141, 576 (1966).

[27]D. L. Martin, Phys. Rev. 170, 650 (1968).

[28]D. L. Martin, Phys. Rev. B 8, 5357 (1974).

[29]W. Marshall, Phys. Rev. 118, 1519 (1960); M. W. Klein and R. Brout, Phys. Rev. 132, 2412 (1963); M. W. Klein, Phys. Rev. 136, A1156 (1964); J. Friedel, J. Phys. Radium 23, 692 (1962); M. W. Klein, Phys. Rev. 173, 552 (1968); J. Souletie and R. Tournier, J. Low Temp. Phys. 1, 95 (1969).

[30]A. W. Overhauser, J. Phys. Chem. Solids 13, 71 (1960); Phys. Rev. 128, 1437 (1962); J. Appl. Phys. 34, 1019 (1963).